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Theory of Solutions of Molecules Containing Widely Separated Charges with Special Application to Zwitterions*

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The electrical contribution to the chemical potential of an ion having an arbitrary charge distribution is calculated with the aid of the Debye-Hückel theory. The calculation is based upon a general solution in polar coordinates of the approximate Debye-Hückel equation, $\Delta\psi - \kappa^2\psi = 0$. In addition, the Born relation between the free energy of solvation of a spherical ion and the dielectric constant of the solvent, is generalized to include ions of arbitrary charge distribution. Application of the theory to a study of the influence of simple electrolytes, and of the dielectric constant of the solvent on the solubilities of the aliphatic amino-acids in alcohol water mixtures, is discussed.

I.

THE aliphatic amino-acids, as well as a number of related compounds, exhibit many of the properties of strong electrolytes when dissolved in solvents of high dielectric constant such as water or alcohol. But unlike electrolytes, they do not appreciably increase the electrical conductivity of the solution. Evidently then, these substances do not produce real ions in solution. To account for this peculiar behavior, Adams[1] and Bjerrum[2] suggested that both the acidic and basic groups of an amino-acid molecule are completely ionized in certain solvents, giving rise to a hybrid ion with no resultant charge. Although it cannot contribute to the conductivity of the solution, the hybrid ion is surrounded by a strong electrostatic field, because of the wide separation of its charged groups. Therefore, large deviations from the ideal solution laws arising from electrostatic interaction between the hybrid ions, the solvent, and real ions present in the solution, might be expected. Hybrid ions of this type have been called Zwitterions.

In recent years much evidence in favor of the Zwitterionic hypothesis has accumulated.[3] Perhaps the most convincing argument in its favor is furnished by measurements of the dielectric constants of amino-acid solutions.[4] The high dielectric constants of these solutions can be explained if one attributes an enormous electric moment of the order of 20×10^{-18} e.s.u. to an α-amino acid molecule and still larger moments to those of the β and γ-acids. Dipole moments of this magnitude could scarcely be produced except by amphoteric ionization leading to the formation of Zwitterions.

In an earlier article, the influence of salts upon the activity of Zwitterions in solution was investigated from the standpoint of the Debye-

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[1] E. Q. Adams, J. Am. Chem. Soc. **38**, 1503 (1916).

[2] N. Bjerrum, Zeits. f. physik. Chemie **104**, 147 (1923).

[3] E. J. Cohn, Ergebnisse der Physiologie **33**, 781 (1931); Naturwiss. **20** (36), 44 (1932).

[4] Hedestrand, Zeits. f. physik. Chemie **135**, 36 (1928); Wyman and McMeekin, J. Am. Chem. Soc. **55**, 915 (1933); **53**, 3292 (1931); Devoto, Gazz. Chim. Ital. **60**, 520 (1930); **61**, 897 (1932).

Hückel theory.[5] Although the theory predicts a large electrical contribution to the chemical potential of a Zwitterion, the logarithm of its activity coefficient is found to contain no term proportional to the square root of the ionic strength of the salt. It was therefore concluded that a Zwitterion behaves more like a highly polar non-electrolyte molecule than like a real ion in salt solutions of low ionic strength. The Zwitterion was represented by a highly simplified model consisting of two oppositely charged spheres with a rigid connection between their centers. This model was chosen because of its close resemblance to two independent ions. It has, however, certain disadvantages from a mathematical point of view. The electrostatic potential in the neighborhood of the Zwitterion is most conveniently expressed in terms of polar coordinates, and the boundary conditions lead to an infinite set of linear equations which are very difficult to solve unless the boundary of the ion has spherical symmetry.

In the present article the influence of salts and of the dielectric constant of the solvent upon the activity of a spherical ion, having a complex charge distribution, is investigated. When the net charge of the complex ion is zero, and its dipole moment is large, it corresponds to a Zwitterion. The discussion is limited to solutions in which the concentration of the complex ions, in particular Zwitterions, is so low that their mutual electrostatic interaction can be neglected. It should be possible to treat the mutual interaction of Zwitterions at least approximately by means of Keesom's theory of dipole gases.[6] This, however, will not be undertaken here.

II.

We consider a solution of complex ions at low concentration in a solvent of dielectric constant D. For the present purposes the ion is schematically represented by sphere of radius b, having a dielectric constant D_i, within which are situated M discrete point charges $e_1 \cdots e_M$. A polar coordinate system with origin at the center of the sphere b may be conveniently employed to describe the configuration of the charges $e_1 \cdots e_M$. The position of each charge e_k is then given by three coordinates r_k, ϑ_k, and φ_k. The orientation of the coordinate system is quite arbitrary, and does not enter into the final result. The electrostatic potential at any point (r, ϑ, φ) inside the sphere b satisfies Laplace's equation and is given by

$$V_1 = \sum_{k=1}^{M} \frac{e_k}{D_i |\mathbf{r} - \mathbf{r}_k|} + \psi$$

$$\psi = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} B_{nm} r^n P_n^m(\cos \vartheta) e^{im\varphi}, \qquad (1)$$

where $|\mathbf{r} - \mathbf{r}_k|$ is the distance of the charge e_k from the point (r, ϑ, φ), and ψ is the contribution to the potential arising from charge distributions in the solution outside of the sphere b. The $P_n^m(\cos \vartheta)$ are the associated Legendre functions and i is the imaginary unit, $(-1)^{\frac{1}{2}}$. The constants B_{nm} are to be determined by the proper boundary conditions. If there is no space charge in the surrounding solution, and the dielectric constant of the ion D_i is identical with that of the solvent D, then ψ vanishes. This, however, is not in general true.

We now suppose that in addition to the complex ions, the solution contains a simple electrolyte which produces ions of the valence types $Z_1 \cdots Z_i$, present at the molal concentrations $C_1 \cdots C_i$. These ions are supposed not only to be spherical in shape, but also to possess spherically symmetrical charge distributions. In other words their multipole electric moments, dipole, quadrupole, etc., are all assumed to be zero. If the mean distance of closest approach of these ions to the complex ion is a, there will exist a second spherical boundary of radius a, concentric with the sphere b, within which no ions penetrate. In the spherical shell, bounded by the spheres a and b, the potential V_2 must therefore satisfy Laplace's equation. When expanded in spherical harmonics it must have the form

$$V_2 = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \{C_{nm}/r^{n+1} + G_{nm} r^n\} P_n^m(\cos \vartheta) e^{im\varphi}, \qquad (2)$$

[5] G. Scatchard and J. G. Kirkwood, Phys. Zeits. **33**, 297 (1932).

[6] W. H. Keesom, Phys. Zeits. **22**, 129, 643 (1921).

where r, ϑ, φ are the coordinates of a point in this region. We also remember that the dielectric constant in this region is D, that of the solvent.

In the solution outside of the sphere a, interaction of the complex ion with the simple electrolyte ions produces a mean space charge. The potential V_3 in this region satisfies Poisson's equation. If we assume that the mean space charge in the neighborhood of the complex ion is given by the Boltzmann distribution formula in the form employed by Debye, and further if nonlinear terms in V_3 appearing in the expansion of the Boltzmann factor are dropped, we may employ the approximate equation of the Debye-Hückel theory to determine this potential.

$$\Delta V_3 - \kappa^2 V_3 = 0, \qquad \kappa^2 = (4\pi N\epsilon^2/1000DkT)\sum_i Z_i^2 C_i, \tag{3}$$

where Δ is the Laplacian operator,* and κ^2 is a function of the ionic strength, $\sum_i Z_i^2 C_i/2$ of the electrolyte, as well as of Avogadro's number N, the electronic charge ϵ, Boltzmann's constant k, the absolute temperature T, and the dielectric constant of the solution D. If we ignore the influence of the electrolyte on the dielectric constant, D is equal to the dielectric constant of the solvent. After separation of variables, a general solution of Eq. (3) in polar coordinates can be effected.[5] All solutions which vanish at infinity, a necessary boundary condition, may be expressed in the form

$$V_3 = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} (A_{nm}/r^{n+1}) e^{-\kappa r} K_n(\kappa r) P_n^m(\cos\vartheta) e^{im\varphi}, \qquad K_n(x) = \sum_{s=0}^{n} \frac{2^s n!(2n-s)!}{s!(2n)!(n-s)!} x^s, \tag{4}$$

where r, ϑ, φ are the coordinates of any point in the solution outside the sphere a, referred to the polar system with origin at the center of this sphere.† The polynomials $K_n(x)$ and their first derivatives $K_n'(x)$ satisfy the following recurrence relations which will later be of use.

$$\begin{aligned} &(2n+1+x)K_n(x) - xK_n'(x) = (2n+1)K_{n+1}(x), \\ &K_{n+1}(x) - K_n(x) = x^2 K_{n-1}(x)/(2n+1)(2n-1); \qquad n>0. \end{aligned} \tag{5}$$

In the three potentials V_1, V_2 and V_3 there are four constants A_{nm}, C_{nm}, G_{nm}, and B_{nm} to be determined for every set of indices n and m. These constants are fixed by the following boundary conditions. On the surface of the sphere a, V_3 and V_2 as well as their gradients shall be equal:

$$\begin{aligned} V_3 &= V_2 \\ &\qquad r=a. \\ \nabla V_3 &= \nabla V_2 \end{aligned} \tag{6}$$

On the surface of the sphere b, V_2 and V_1, the tangential components of their gradients, and the normal components of the dielectric displacement (dielectric constant multiplied by the field strength) shall be equal.[7]

$$\begin{aligned} &V_2 = V_1; \qquad \frac{1}{r}\frac{\partial V_2}{\partial \vartheta} = \frac{1}{r}\frac{\partial V_1}{\partial \vartheta} \\ &\frac{1}{r\sin\vartheta}\frac{\partial V_2}{\partial \varphi} = \frac{1}{r\sin\vartheta}\frac{\partial V_1}{\partial \varphi}; \qquad r=b \\ &D\frac{\partial V_2}{\partial r} = D_i\frac{\partial V_1}{\partial r}. \end{aligned} \tag{7}$$

* For example in polar coordinates

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}.$$

† The radial factors of the solutions of Eq. (3) are related to the Bessel functions $r^{-\frac{1}{2}}I_{n+\frac{1}{2}}(\kappa r)$ or $r^{-\frac{1}{2}}J_{n+\frac{1}{2}}(i\kappa r)$. However, these functions as customarily defined do not satisfy the boundary conditions of the present problem.

[7] See for example Abraham-Becker, *Theorie der Elektrizität*, I, §32, p. 72.

Since some of them are equivalent, relations (6) and (7) furnish just four independent conditions. Before applying them we note that the first part of the potential V_1 may be expanded in spherical harmonics in the following form in the neighborhood of the surface of the sphere b, provided all of the r_k are less than b.

$$\sum_{k=1}^{M} \frac{e_k}{D_i|\mathbf{r}-\mathbf{r}_k|} = \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \frac{E_{nm}}{D_i r^{n+1}} P_n^m(\cos\vartheta) e^{im\varphi}, \tag{8}$$

where

$$E_{nm} = [(n-|m|)!/(n+|m|)!] \sum_{k=1}^{M} e_k r_k^n P_n^m(\cos\vartheta_k) e^{-im\varphi_k}. \tag{9}$$

We now apply the boundary conditions, which are at once seen to be satisfied independently by every harmonic component of the potentials. For every set of indices m and n, four equations are obtained:

$$\begin{gathered} A_{nm} e^{-\kappa a} K_n(\kappa a) = C_{nm} + a^{2n+1} G_{nm}, \\ A_{nm} e^{-\kappa a}[(n+1+\kappa a) K_n(\kappa a) - \kappa a K_n'(\kappa a)] = (n+1) C_{nm} - n a^{2n+1} G_{nm}, \\ E_{nm}/D_i + b^{2n+1} B_{nm} = C_{nm} + b^{2n+1} G_{nm}, \\ (n+1) E_{nm} - n D_i b^{2n+1} B_{nm} = (n+1) D C_{nm} - n D b^{2n+1} G_{nm}. \end{gathered} \tag{10}$$

Solution of these equations and use of the recurrence formulas (5) lead to the following expression for the constants B_{nm}, which are the only ones we require

$$\begin{aligned} B_{nm} = {} & \frac{E_{nm}}{D_i b^{2n+1}} \frac{(n+1)(D_i - D)}{(n+1)D + n D_i} \\ & - \frac{E_{nm}}{D a^{2n+1}} \frac{2n+1}{2n-1} \left[\frac{D}{(n+1)D + n D_i}\right]^2 \frac{\kappa^2 a^2 K_{n-1}(\kappa a)}{K_{n+1}(\kappa a) + \dfrac{n(D-D_i)}{(n+1)D + n D_i} \left(\dfrac{b}{a}\right)^{2n+1} \dfrac{\kappa^2 a^2 K_{n-1}(\kappa a)}{(2n-1)(2n+1)}} \end{aligned} \tag{11}$$

except for $n=0$, where

$$B_{00} = \frac{E_{00}}{b}\left(\frac{1}{D} - \frac{1}{D_i}\right) - \frac{E_{00}}{Da} \frac{\kappa a}{1+\kappa a}.$$

It is to be noted that only B_{00} contains a term proportional to κ, the square root of the ionic strength. In every other B_{nm} the lowest power of κ is the second.

The mutual electrostatic energy of the complex ion and the medium in which it is immersed arises from the ionic space charge in the solution outside the sphere a, and from a surface charge of polarization on the sphere b depending upon the difference between D_i and D. This energy is determined by the potential ψ, the second term of Eq. (1). It can therefore be expressed as a function of the B_{nm} of Eq. (11), upon which ψ depends. It is easily verified that the B_{nm} are linear functions of the charges $e_1 \cdots e_M$, constituting the ion, so that ψ also is a linear function of these charges. By a hypothetical charging process of the Guntelberg-Müller type, one finds that the mutual electrostatic energy of the ion and the medium, equal to a work of charging, is given by one-half the sum of the products of each e_l by the value of ψ at the point $(r_l, \vartheta_l, \varphi_l)$.*

$$W = \tfrac{1}{2} \sum_{l=1}^{M} e_l \psi(r_l, \vartheta_l, \varphi_l). \tag{12}$$

Introducing ψ from Eq. (1) and using the values of B_{nm} given by Eq. (10), we obtain

* Self-energy terms for the charge distribution $e_1 \cdots e_M$ are omitted. They arise from the first term of V_1 and are independent of the medium. Further, because of the crudity of the molecular model, they have no physical significance.

$$W = W_0 + W(\kappa),$$

$$W_0 = \tfrac{1}{2}\sum_{n=0}^{\infty} \frac{(n+1)Q_n(D_i - D)}{D_i b^{2n+1}[(n+1)D + nD_i]},$$

$$W(\kappa) = -(Q_0/2D)\kappa/(1+\kappa a) \tag{13}$$

$$-\tfrac{1}{2}\sum_{n=1}^{\infty} \frac{Q_n}{Da^{2n-1}} \frac{2n+1}{2n-1}\left[\frac{D}{(n+1)D+nD_i}\right]^2 \frac{\kappa^2 K_{n-1}(\kappa a)}{K_{n+1}(\kappa a) + \dfrac{n(D-D_i)}{(n+1)D+nD_i}\left(\dfrac{b}{a}\right)^{2n+1} \dfrac{\kappa^2 a^2 K_{n-1}(\kappa a)}{(2n-1)(2n+1)}},$$

$$Q_n = \sum_{k=1}^{M}\sum_{l=1}^{M} e_k e_l r_k{}^n r_l{}^n \sum_{m=-n}^{+n} \frac{(n-|m|)!}{(n+|m|)!} P_n{}^m(\cos\vartheta_k) P_n{}^m(\cos\vartheta_l) e^{im(\varphi_k - \varphi_l)}.$$

By the addition theorem of spherical harmonics, the Q_n may be written more simply as

$$Q_n = \sum_{k=1}^{M}\sum_{l=1}^{M} e_k e_l r_k{}^n r_l{}^n P_n(\cos\vartheta_{kl}), \tag{14}$$

where the $P_n(\cos\vartheta)$ are the ordinary Legendre functions and ϑ_{kl} is the angle between r_k and r_l, the lines drawn from the center of the sphere b to the charges e_k and e_l. Thus the final expression is independent of the orientation of the coordinate system (r, ϑ, φ). The early members of the function system $P_n(x)$ have the form

$$\begin{aligned} P_0(x) &= 1, \\ P_1(x) &= x, \\ P_2(x) &= (3x^2-1)/2, \\ P_3(x) &= (5x^3-3x)/2. \end{aligned} \tag{15}$$

Thus we find that Q_0 is simply $(\sum_k e_k)^2$ or $Z^2\epsilon^2$ where Z is the valence of the complex ion. The terms in Eq. (13), corresponding to $n=0$, are seen to be identical with those of the ordinary Debye-Hückel theory, applied to an ion having a spherically symmetric charge distribution. If the net charge of the complex ion is zero, in which case it would correspond to a hybrid ion, the term for $n=0$ vanishes and the first term of importance is the one involving Q_1. Q_1 is readily seen to be equal to the square of the dipole moment of the ion. The succeeding Q_n's involve the higher order multipole moments.

It should be remarked here that the foregoing analysis is in no way restricted to ions consisting of discrete point charges e_k. A slight modification of the argument permits one to treat a complex ion whose charge distribution is a continuous function of position, $\rho_0(r, \vartheta, \varphi)$. Since we are interested here only in electrostatic contributions to the energy and do not take van der Waals forces into account, we may use a ρ_0 averaged over the high frequency motion of the electrons. Appropriate distribution functions of this type have been calculated with the aid of quantum mechanics by Hartree.[8] If ρ_0 is known the potential inside the ion must satisfy Poisson's equation

$$\Delta V_1 = -4\pi\rho_0. \tag{16}$$

The solution of this equation which replaces the V_1 of Eq. (1) is

$$V_1 = \int \frac{\rho_0(r', \vartheta', \varphi')}{|\mathbf{r}' - \mathbf{r}|} dv' + \psi, \tag{17}$$

where ψ is the same function as before, and the integration is extended over all of space. Actually, we may suppose $\rho_0(r, \vartheta, \varphi)$ to be effectively zero outside of a sphere of radius b. The potentials outside of the sphere b remain the same as before, and the same expression for W, Eq. (13), is obtained, except that the Q_n's are now given by integrals of the form

$$Q_n = \int\int \rho_0(r, \vartheta, \varphi)\rho_0(r', \vartheta', \varphi') r^n r'^n \times P_n[\cos(\vartheta - \vartheta')] dv' dv \tag{18}$$

instead of by sums over discrete point charges. One would still want to represent the atomic nuclei by point charges, so that in general the Q_n's would consist of an integral over the

[8] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).

electronic distribution and a discrete sum over the nuclear point charges. For the present purposes, this generalization is unimportant, since we do not try to calculate the multipole moments Q_n explicitly from atomic structure. However, it is of interest to know that the results have the same form, whether we employ the crude point charge model or a more refined one, consistent with modern theories of molecular structure.

We may inquire as to the significance of the dielectric constant of the ion D_i. By assigning a value greater than unity to D_i, we have a crude means of taking the polarization of the ion into account. Henceforth we shall neglect this effect and assign a value unity to D_i. Further, since we shall be interested in solutions having dielectric constants greater than 25, we may simplify our formulas by neglecting D_i/D in comparison with unity, without introducing much error.

We are now able to calculate the change in the chemical potential of a complex ion attending its transfer from one solution to another, under the assumption that this change is equal to the difference between the works of charging, Eq. (13), in the two mediums. If we choose a standard state as a solution in which the chemical potential of the complex ion is μ^0, the activity coefficient, γ, in a second solution, in which the chemical potential is μ, is defined by the relation

$$\mu-\mu^0=kT\log\gamma x/x^0$$
$$=kT\log\gamma+kT\log x/x^0, \quad (19)$$

where x^0 and x are the mol fractions of the complex ion type in the respective solutions. If in addition to the ideal term $kT\log x/x^0$, the only change in chemical potential is assumed to be that associated with electrostatic forces, we have

$$\log\gamma=(W-W^0)/kT, \quad (20)$$

where W and W^0 are the respective works of charging in the two solutions.

We shall first investigate the influence of simple electrolytes on the activity coefficient of the complex ion. We choose the standard state as a solution in which the ionic strength of the simple electrolyte is zero, and the concentration of the complex ions is sufficiently small to allow the neglect of their mutual interactions. From Eqs. (13) and (20) we obtain the following expression for $\log\gamma$ in a solution containing the simple electrolyte at an ionic strength proportional to κ^2, under the assumption that the dielectric constant of the solution is that of the pure solvent, D, and that the concentration of the complex ions remains small.*

$$\log\gamma=W(\kappa)/kT=-(Q_0/2DkT)\kappa/(1+\kappa a)$$
$$-\frac{\kappa^2}{2DkT}\sum_{n=1}^{\infty}\frac{(2n+1)Q_n}{(2n-1)(n+1)^2a^{2n-1}}\frac{K_{n-1}(\kappa a)}{K_{n+1}(\kappa a)+\dfrac{nb^{2n+1}\kappa^2K_{n-1}(\kappa a)}{(n+1)(2n-1)(2n+1)a^{2n-1}}}. \quad (21)$$

* The fact that we have employed the Guntelberg-Müller charging process rather than that of Debye perhaps requires some comment. The Guntelberg-Müller process yields the chemical potential of the complex ion directly, while the Debye process requires an intermediate calculation of the total free energy of the solution (complex ions and simple electrolyte). We cannot calculate the total free energy statistically, without first investigating the influence of complex ions upon the potential in a simple electrolyte ion. This problem is somewhat more complicated than that of the influence of the simple electrolyte on the potential in a complex ion. So far it has not been solved by means of the Debye theory.

We may assume that the two charging processes lead to the same result if the condition of integrability is fulfilled. If ψ_i is the potential in a simple electrolyte ion i, and ψ_s is the potential in a complex ion s, this principle requires that

$$\partial\psi_s/\partial e_i=\partial\psi_i/\partial e_s,$$

where e_i is the charge on the ion i, and e_s is a common factor of the ensemble of charges making up the complex ion. It should be pointed out that e_i refers to the charge on a single ion i, and not to the charge of the ion type. (Onsager, Chem. Rev. **13**, 73 (1933); Halpern, J. Chem. Phys. **2**, 85 (1934).) Since solutions of the Debye linear equation, Eq. (3), generally satisfy the condition of integrability, we might reasonably suppose that the integrability condition is satisfied, without explicitly calculating ψ_i.

It is nevertheless interesting to investigate the matter further by means of a semi-thermodynamic argument suggested to the writer by Professor Scatchard. Without reproducing the argument in detail, we shall give an

In this expression, the above-mentioned approximation of neglecting D_i in comparison with D has been introduced. It is perhaps worth while at this point to give explicit expressions for some of the polynomials $K_n(x)$. We have from Eq. (4)

$$\begin{aligned} K_0(x)&=1,\\ K_1(x)&=1+x,\\ K_2(x)&=1+x+x^2/3,\\ K_3(x)&=1+x+2x^2/5+x^3/15,\\ K_4(x)&=1+x+3x^2/7+2x^3/21+x^4/105. \end{aligned} \tag{22}$$

If we are interested in the influence of the simple electrolyte upon the solubility of Zwitterions, we have

$$\log (N/N_0)=-\log \gamma, \tag{23}$$

where N_0 is the solubility at zero ionic strength of the simple electrolyte, and N is the solubility at a finite ionic strength. The solubilities are to be expressed as mol fractions.

The influence of the complex ions upon the activity of a simple electrolyte ion may be obtained in a similar manner. We treat only the case in which the complex ion is a Zwitterion ($Q_0=0$), and the ionic strength of the electrolyte is very small. Under these conditions, each of the polynomials $K_n(\kappa a)$ is closely approximated by unity. Moreover, the mutual interaction of the electrolyte ions can be

outline of it for the case when the complex ion is a Zwitterion. At Zwitterion concentrations sufficiently small that may neglect the dependence of the chemical potential, μ_z, on the Zwitterion concentration, we may write by thermodynamics

$$F=F_0+\int_0^{n_z}\mu_z dn_z=F_0+n_z\mu_z,$$

where F is the electrical free energy of the solution, F_0 the electrical free energy of the simple electrolyte solution in the absence of Zwitterions, μ_z the electrical part of the chemical potential of a Zwitterion, and n_z their number. The potential ψ_i in an ion may then be calculated from F by the following relation:

$$\psi_i=\partial F/\partial e_i=\psi_i^0+n_z\partial\mu_z/\partial e_i,$$
$$\psi_i^0=-(e_i/D)\kappa/(1+\kappa a_i).$$

To avoid undue complication, we neglect small terms in the denominators of Eq. (22) depending on $(b/a)^{2n+1}$, and write

$$\mu_z-\mu_z^0=kT\log\gamma_z=-\frac{\kappa^2}{2D}\sum_{n=1}^{\infty}\frac{(2n+1)Q_n}{(2n-1)(n+1)^2a^{2n-1}}\frac{K_{n-1}(\kappa a)}{K_{n+1}(\kappa a)}.$$

Differentiation with respect to e_i and multiplication by n_z yields

$$\psi_i=-(e_i/D)\kappa/(1+\kappa a_i)-\frac{4\pi e_i n_z}{D^2kTv}\left\{\frac{3}{4}\frac{Q_1}{a}\frac{1-\kappa a/2+\kappa^2a^2(1+\kappa a)/6}{1+\kappa a+\kappa^2a^2/3}\right.$$
$$\left.+\sum_{n=2}^{\infty}\frac{(2n+1)Q_n}{(2n-1)(n+1)^2a^{2n-1}}\frac{K_{n-1}(\kappa a)+\kappa^2a^2[K_n(\kappa a)/(2n+1)-K_{n-2}(\kappa a)/(2n-1)]}{K_{n+1}(\kappa a)}\right\}.$$

The limiting form of this expression is used in the following section to obtain the influence of Zwitterions on the activity of slightly soluble salts.

The above value of ψ_i automatically fulfills the condition of integrability, when μ_z is calculated by the Guntelberg process, but it would be arguing in a circle to say that we have proved that the integrability condition is satisfied by this calculation. However, we can get at the matter in another way. Thus the chemical potential of the ion i is given by $\mu_i=\mu_i^0+n_z(\partial\mu_z/\partial n_i)$. By the Guntelberg process,

$$\psi_i=\partial\mu_i/\partial e_i=\psi_i^0+n_z(\partial^2\mu_z/\partial e_i\partial n_i).$$

The ψ_i calculated by this relation agrees with the above expression to terms of order $1/n_i$, where n_i is the number of ions of the ith type present. Thus the two calculations of ψ_i agree except for a quantity of completely negligible order. Applying the condition of integrability to the latter expression for ψ_i, we find that it requires $\partial\psi_z/\partial e_i=\partial^2\psi_z/\partial e_i\partial n_i$. We find that this condition is fulfilled by our ψ_z with the neglect of terms of order $1/n_i$, due to the fact that ψ_z is of the form $e_zf(\kappa)$. It should be remarked that this would not be true for an arbitrary ψ_z, for example, one containing terms of the Gronwall-La Mer type. Thus we have shown that the Guntelberg process gives a result which is consistent with the integrability condition, in the present case. Although the question cannot be definitely settled without an independent statistical calculation of ψ_i we may assume with some confidence that our result is independent of the charging process.

ignored. Choosing the standard state of the electrolyte as a solution in which the Zwitterion concentration is zero, we have for the activity coefficient of an ion of type i in a solution containing Zwitterions at a molal concentration C,

$$\log \gamma_i = -\frac{2\pi N Z_i^2 \epsilon^2}{1000 D^2 k^2 T^2} C \sum_{n=1}^{\infty} \frac{(2n+1)Q_n}{(2n-1)(n+1)^2 a^{2n-1}}. \tag{24}$$

This expression is useful in determining the influence of Zwitterions on the solubility of a slightly soluble salt. If N is the solubility of the salt in a solution containing Zwitterions, and N_0 is its solubility in the absence of Zwitterions, we have

$$\log (N/N_0) = -\log \gamma_{\pm} = -(1/\sum_i \nu_i)\sum_i \nu_i \log \gamma_i, \tag{25}$$

where $\gamma\pm$ is the mean activity coefficient of the salt ions, and ν_i is the number of ions of the ith type produced by a salt molecule.

We now turn our attention to the influence of the dielectric constant of the solvent upon the chemical potential of the complex ion, in the absence of the electrolyte. In this case κ vanishes and W reduces to the first term, W_0, of Eq. (12). If we choose as the standard state a solution of the complex ion at low concentration in a solvent of dielectric constant D_0, we have from Eqs. (13) and (20),

$$\log \gamma = \frac{1}{2kT} \sum_{n=0}^{\infty} \frac{(n+1)Q_n}{b^{2n+1}} \left\{ \frac{1-D}{(n+1)D+n} - \frac{1-D_0}{(n+1)D_0+n} \right\} \tag{26}$$

as the expression for the activity coefficient in a solvent of dielectric constant D. Here again the dielectric constant of the complex ion has been assigned the value unity. The first term of Eq. (26) corresponds to Born's result for an ion having a spherically symmetrical charge distribution.[9] The remaining terms depend upon the multipole electric moments of the ion. For the ratio of the solubilities N and N_0 of Zwitterions in solvents having the respective dielectric constants D and D_0, we may write

$$\log (N/N_0) = -\log \gamma, \tag{27}$$

where $\log \gamma$ is given by Eq. (26). The rate of change of $\log (N/N_0)$ with the reciprocal dielectric constant is

$$\frac{d \log (N/N_0)}{d(1/D)} = -\frac{1}{2kT} \sum_{n=1}^{\infty} \frac{2n+1}{n+1} \frac{Q_n}{b^{2n+1}} \frac{1}{(1+n/(n+1)D)^2}. \tag{28}$$

Thus, as long as D is large, we may expect $\log (N/N_0)$ to be virtually a linear function of $1/D$.[10]

III.

We should expect Eqs. (21) and (26) to provide a refinement of the simple Debye-Hückel theory in the case of real ions possessing asymmetric charge distributions. Here, however, the terms depending upon the multipole moments of the ion would in general be of the nature of small corrections to the initial terms, depending

[9] M. Born, Zeits. f. Physik **1**, 45 (1920).

[10] R. P. Bell, Trans. Faraday Soc. **27**, 797 (1931), has obtained an equation corresponding to Eq. (26) for the influence of the solvent dielectric constant on the chemical potential of a dipole molecule. Bell's expressions for the electrostatic potentials near the boundary of the molecule agree with the dipole terms ($n=1$) of our potentials in the limit $\kappa=0$. However, his value for the electrostatic energy of the dipole differs from ours by a factor $\frac{1}{3}$. To obtain the electrostatic energy, he integrates $DE^2/8\pi$ over all of space. This should and does give the same result as summing $\frac{1}{2}e\psi$ over all charges of the molecule, where ψ is the potential in the interior of the molecule due to external charge distributions. Bell's factor $\frac{1}{3}$ appears to arise from a faulty estimate of $\int DE^2/8\pi dv$ in the interior of the molecule. Thus he extends the integral over the volume occupied by the charges constituting the dipole, which is not permissible, and also uses an expression for the potential which does not converge near these charges.

upon the net charge. In the case of Zwitterions on the other hand, the total charge is zero, and the terms of Eqs. (21) and (26) containing Q_0 vanish. Thus the entire electrical contribution to the chemical potential arises from the multipole moments. For this reason, Eqs. (21) and (26) find their most interesting application to the case of Zwitterions. Of course the present theory is highly simplified and could only be expected to give precise results if the following conditions were exactly fulfilled. (1) The Zwitterions have spherical boundaries. (2) They are present in the solution at such low concentration that their mutual interaction is negligible. (3) Their multipole electric moments are very large relative to those of a solvent molecule. (4) Non-electrostatic deviations from the ideal solution laws are insignificant. (5) Corrections of the Gronwall-La Mer type arising from nonlinear terms in the Poisson-Boltzmann equation can be neglected. However, it often happens that these conditions are approximately fulfilled, so that our equations furnish the basis for a semi-quantitative theory of Zwitterionic solutions.

According to the Zwitterionic hypothesis, the aliphatic amino acids exist as hybrid ions in solvents of high dielectric constant. Thus an α-amino acid $RNH_2CHCOOH$ forms a Zwitterion of the structure $RNH_3^+CHCOO^-$. The simplest member of this class of substances is glycine which forms the Zwitterion $NH_3^+CH_2COO^-$. Among the aliphatic amino acids, glycine furnishes the most favorable example for the application of the present theory. Not only may the nonelectrostatic deviation from the ideal solution laws be expected to be a minimum, but also the boundary of the glycine Zwitterion can be roughly approximated by a spherical surface. This is not obvious from the formula, but examination of a steric model makes it plausible. An extensive experimental study of the solubility relations of the aliphatic amino acids in alcohol-water mixtures has been carried out by E. J. Cohn and his co-workers.[11] Professor Cohn has kindly placed at our disposal his data, in part unpublished, relating to the influence of salts and

[11] E. J. Cohn, Naturwiss. **20**, 44 (1932).

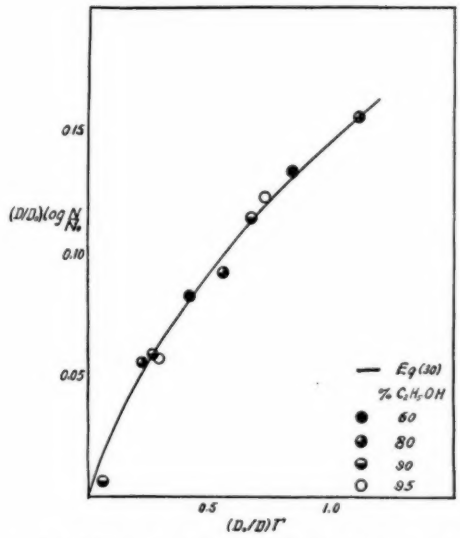

FIG. 1. Solubility of glycine in alcohol-water mixtures containing LiCl at 25°C.

of the dielectric constant of the solvent upon the solubility of glycine.

An interesting property of Eq. (21) provides a means of correlating measurements of the influence of salts on the solubility of glycine in different solvents. By definition, Eq. (3), κ^2 is proportional to Γ/D, where Γ, the ionic strength of the salt, is defined as $\sum_i Z_i^2 C_i/2$. Thus according to Eq. (21), $D \log \gamma$ or $D \log (N/N_0)$ should be the same function of Γ/D for all solvents. This conclusion is confirmed by Cohn's measurements at 25°C of the solubility of glycine in alcohol-water mixtures containing lithium chloride. In Fig. 1, the experimental values of $(D/D_0) \log (N/N_0)$ in solutions of alcohol content varying from sixty to ninety-five percent, are plotted as a function of $(D_0/D)\Gamma$. The dielectric constant, D_0, of water at 25° has been introduced merely as a convenient scale factor. It is seen that the points fall very nearly upon a single curve up to ionic strengths, which doubtless lie beyond the region of validity of the present theory. Measurements in pure water do not fall upon the curve. This, however, is not to be expected. While the absolute solubility of glycine in solutions of high alcohol content is very low, its solubility in solutions of high water content is so high that the mutual interaction of the glycine hybrid ions can no longer be neglected, and Eq. (21) is no longer applicable.

Unless the charge distribution is concentrated very near the boundary of the ion, the sums in Eq. (21) and Eq. (26) converge quite rapidly, so that it is only necessary to retain the first few terms. For a Zwitterion, Q_0 is of course zero, while Q_1 is equal to the square of the dipole moment μ, and is independent of the position of the electric center of the charge distribution. The constants Q_2, Q_3, etc., are functions of the higher order multipole moments. They depend not only upon the relative charge distribution, but also upon the distance of the electric center from the boundary of the ion. If we approximate the charge distribution of a simple Zwitterion by two point charges $+e$ and $-e$ separated by a distance R, and situated at equal distances r from the center of the boundary sphere b, the constants Q_n have the following values

$$\begin{aligned} Q_0&=0,\\ Q_1&=\mu^2=\epsilon^2R^2,\\ Q_2&=3\mu^2[r^2-R^2/4],\\ Q_3&=6\mu^2[r^4-5r^2R^2/8+5R^4/48]. \end{aligned} \tag{29}$$

The Q_n of higher order may be calculated without difficulty from Eq. (14), for this or for any other simple charge distribution. If we neglect terms involving Q_n of higher order than the second, we obtain from Eqs. (21) and (23), after converting to common logarithms

$$(D/D_0)\log_{10}N/N_0=A\Gamma'\left\{\frac{Q_1}{a}\frac{1}{1+(B\Gamma')^{\frac{1}{2}}+[1+\frac{1}{2}(b/a)^3]B\Gamma'/3}\right.$$
$$\left.+\frac{20}{81}\frac{Q_2}{a^3}\frac{1+(B\Gamma')^{\frac{1}{2}}}{1+(B\Gamma')^{\frac{1}{2}}+2[1+(1/9)(b/a)^5]B\Gamma'/5+[1+\frac{2}{3}(b/a)^5](B\Gamma')^{\frac{1}{2}}/15}\right\}$$
$$A=3\pi N\epsilon^2/2303D_0^2k^2T^2=(3.00\times10^{34})/D_0^2T^2, \tag{30}$$
$$B=8\pi N\epsilon^2a^2/1000D_0kT=2.53\times10^{19}(a^2/D_0T),$$
$$\Gamma'=(D_0/D)\Gamma$$

where Q_1 and Q_2 are given by Eq. (29), and the remaining symbols have their usual significance.

In the case of glycine, it is sufficient to retain only the first term of Eq. (30). With a proper choice of the constants Q_1, a and b, Eq. (30) yields the curve of Fig. 1, which fits the experimental points very satisfactorily. The radius, b, of the glycine hybrid ion is estimated from the partial molal volume to lie between 2.6 and 2.8A, depending upon whether a correction for the electrostriction of the solvent is made or not.[12] We therefore assign it a value of 2.7A. The course of the solubility curve is very insensitive to the explicit value of b, being chiefly determined by Q_1 and a. The limiting slope is determined by the ratio Q_1/a and the curvature by a. From the curve, Fig. 1, we obtain a value, 15.0×10^{-18} e.s.u. for the dipole moment, μ, of the glycine Zwitterion, and a value, 3.3A for the mean radius, a, of the salt ions and the Zwitterion. This value of the dipole moment differs but little from Wyman's estimate, 20×10^{-18} e.s.u., based upon measurements of the dielectric constants of an α-amino acid solution.[13] If we divide μ by the electronic charge, we obtain a value, 3.17A, for the effective separation of the positive charge on the basic group and the negative charge on the acidic group of the glycine Zwitterion. From a steric model of glycine, one finds that if the center of gravity of the positive charge is on the nitrogen atom of the amino group and that of the negative charge lies between the oxygen atoms of the carboxyl group, this distance should be about 3.3A. Due to internal polarization of the molecule, the effective separation of the two charges should certainly be less than this. Thus the value, 3.17A, obtained from solubility data with the aid of Eq. (30) furnishes a very reasonable estimate of the effective separation of the charged groups, although it is probably somewhat too large.

[12] E. J. Cohn, Science **79**, 83 (1934).

[13] J. Wyman, J. Am. Chem. Soc. **56**, 536 (1934).

We now turn our attention to the influence of the dielectric constant of the solvent upon the solubility of glycine in the absence of salts. If multipoles of higher order than the quadrupole are neglected and common logarithms are introduced, Eq. (28) becomes

$$\frac{d\log_{10}(N/N_0)}{d(1/D)} = -\frac{2.374\times10^{15}}{T}\left\{\frac{Q_1}{b^3}\frac{1}{(1+1/2D)^2} + \frac{10}{9}\frac{Q_2}{b^5}\frac{1}{(1+2/3D)^2}\right\}. \quad (31)$$

If $\log (N/N_0)$ were plotted as a function of D^{-1}, the slope of the resulting curve should, according to Eq. (31), be independent of the choice of standard state. Moreover, in solvents of dielectric constant greater than that of alcohol, the factors $(1+n/(n+1)D)^{-2}$ vary only slightly from unity. Thus in alcohol-water mixtures, the curve, although slightly concave upward, should differ very little from a straight line. Cohn's measured values of $\log (N/N_0)$ for glycine in alcohol water mixtures at 25°C do not exhibit exactly this type of curve when plotted against $1/D$. In solvents rich in water, the curvature, although in the same direction, is much larger than could be accounted for by Eq. (31). This is probably due to mutual interaction of the glycine Zwitterions, not taken into account in this equation. In solvents rich in alcohol, on the other hand, there is a slight downward curvature not predicted by Eq. (31). This is probably due to a selective effect of the glycine Zwitterion upon the molecules of the mixed solvent, which would tend to make the solution in its immediate neighborhood richer in water than the bulk of the solution. This effect is also neglected in Eq. (31). However, in solvents ranging in alcohol content from forty to eighty percent, the slope is nearly constant, and has a mean value -96.4. If the quadruple term is neglected, and Eq. (31) is provisionally applied, this slope should be proportional to Q_1/b^3. Using the value of Q_1 previously obtained from the solubility of glycine in salt solutions, we calculate a value, 2.6A, for the radius b of the glycine Zwitterion. This is in good agreement with the estimates of this quantity from the molal volume, which range from 2.6 to 2.8A. The difference, $a-b$, equal to 0.7A, furnishes an estimate of the effective radii of the lithium and chloride ions. If a^{-1} is calculated as the mean reciprocal of b and ionic radii obtained from crystal structure data, this difference, $b-a$, should be about 1A instead of 0.7A. This discrepancy could be removed by assigning a value, 3.6A, to a, instead of 3.3A. If this were done, the dipole moment calculated from the limiting slope of the salt curve, Fig. 1, would become 15.7×10^{-18} e.s.u., differing from the previous value by only five percent. However, the theoretical curve would then fall below the experimental points at the higher ionic strengths. This latter difficulty could perhaps be removed by taking the influence of higher multipole moments and the effect of the salt on the dielectric constant into account. However, such refinements do not seem worth while, in view of other approximations in the theory, such as the neglect of van der Waals forces and of the selective effect of the Zwitterion on the mixed solvent.

From the foregoing discussion, it is seen that the present theory gives an approximate account of the solubility relations of glycine in alcohol-water mixtures, both in the presence and in the absence of salts, as long as the glycine concentration is small. Moreover, it yields values of the dipole moment and of the size of the glycine Zwitterion, which are of reasonable magnitude. The calculated value of the dipole moment, 15×10^{-18} e.s.u., although it may be in error by fifteen or twenty percent, is perhaps the most reliable estimate as yet available. The theory also gives the qualitative aspects of the solubility relations of the other aliphatic amino acids, although, due to their hydrocarbon chains, the boundaries of these molecules cannot be approximated by spherical surfaces. Moreover, there is evidence that nonelectrostatic deviations from ideality in alcohol-water solutions of these acids increase with the length of the hydrocarbon chain. Quantitative agreement with the present theory is therefore not to be expected.

In conclusion, the writer wishes to acknowledge his indebtedness to Professor George Scatchard and to Professor E. J. Cohn for their interest and cooperation in this work.

The Inter-Relations of Hydrogen and Deuterium Molecules

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It has been shown that neither stopcock grease nor water in a Pyrex or soft-glass vessel affect the concentration of hydrogen-deuterium mixtures. Diffusion through palladium gives a concentration of the isotopes which is about that to be expected from an atomic diffusion process. Desorption from charcoal at liquid air temperatures gives the concentration effect to be expected from a diffusion as molecules. Mercury, Pyrex and soft-glass surfaces at room temperature and charcoal at liquid air temperatures do not promote the reaction between hydrogen and deuterium. Chromium oxide and nickel-kieselguhr surfaces promote the reaction between hydrogen and deuterium in the temperature range between −190° and 110°C. A palladium surface catalyzes the reaction at 270°C. Experimental values have been obtained for the equilibrium constant of the reaction between hydrogen and deuterium from the temperature of liquid air upwards, in accord with theoretical calculations by Urey and Rittenberg based on statistical mechanics.

WITH the discovery of the heavy isotope of hydrogen, the chemist had available a powerful tool for the investigation of fundamental problems in chemistry. For the purpose of exploring the possibilities of the use of this tool, the following investigations were undertaken. Methods had to be devised for the storage of the gas such that the concentration of hydrogen-deuterium mixtures would remain constant over long periods of time. Before any extensive investigation could be conducted, it was essential that a method be developed for the accurate analysis of gas mixtures containing the three possible molecular species, H_2, D_2 and HD. After the completion of these preliminary experiments and others which eliminated possible sources of error, an investigation was undertaken of the interaction of hydrogen and deuterium at catalytic surfaces the characteristics of which were already known. The quantitative aspects of this reaction permit important conclusions to be drawn as to the type of adsorption processes operative under these conditions. Although various methods had already been discovered for the separation of these two isotopes of hydrogen, interest attached to the investigation of alternative methods of concentration which would be informative as to the nature and mechanism of the processes involved. In the following pages a record of these will be found.

I. METHOD OF ANALYSIS

The method of analysis chosen must be capable of distinguishing the three molecular species possible in a mixture of hydrogen and deuterium, namely, H_2, D_2 and HD. Moreover, the instrument must not cause reaction among these molecules. The mass-spectrograph described by Bleakney[1] fulfills these requirements very well. Bleakney[2] has also given methods by which the mass-spectrograph may be applied to the study of hydrogen isotopes. Briefly, the method is to bombard the sample of gas with electrons of controlled potential and to measure the intensity of the positive ions of different masses which are so produced. A mixture of hydrogen and deuterium may form monatomic, diatomic and triatomic ions of masses varying from one to six. The different ions are given in Table I.

TABLE I. *Types of positive ions.*

Mass	1	2	3	4	5	6
Ion	H^+	$(HH)^+$ D^+	$(HHH)^+$ $(HD)^+$	$(DD)^+$ $(DHH)^+$	$(DDH)^+$	$(DDD)^+$

Bleakney[3] and Smyth[4] have discussed the theory of the hydrogen molecule and the probabilities of ionization. The problem is to separate ions of the same mass. The velocity of the electrons producing ionization may be so adjusted that monatomic ions are not produced as primary products and, consequently, are present only to a small extent. Diatomic ions

[1] W. Bleakney, Phys. Rev. **40**, 496 (1932).
[2] W. Bleakney, Phys. Rev. **41**, 32 (1932).
[3] W. Bleakney, Phys. Rev. **35**, 1180 (1930).
[4] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).

may be distinguished from triatomic ions by studying the intensity of the ions as a function of pressure. For example, if we consider the ions of mass 3, the intensity of the $(HD)^+$ ions is proportional to the first power of the pressure while the intensity of the $(HHH)^+$ ions is proportional to the second power of the pressure. If I is the ionic intensity and p the pressure, a plot of I/p *versus* p should give a straight line whose intercept on the I/p axis represents the intensity due to the diatomic ion $(HD)^+$. In this way the various ions may be identified and their relative concentrations determined.

The hydrogen was admitted to the positive ray apparatus through a fine capillary leak while a rapid diffusion pump exhausted this chamber at such a rate that the pressure maintained there was of the order of 10^{-5} mm Hg. This pressure could be regulated by adjusting the pressure of the source or the pumping speed. The lighter molecules will diffuse through the capillary leak faster than the heavier ones but they will also diffuse out through the pumps faster and the assumption is made that these two effects balance each other. The rate of flow through the spectrograph was so rapid that the tungsten filament was not appreciably effective in causing reaction among the molecules.

II. Storage of Gas

Effect of water

Before any kind of comprehensive investigation could be carried out, it was necessary to devise a method for storing quantities of hydrogen-deuterium mixtures under conditions such that the concentration of the mixture would remain constant over long periods of time. Water at once suggested itself for use as a containing fluid, but there arose the possibility of an interchange between the deuterium in the gas phase and the hydrogen atoms in water. Such a process would decrease the concentration of deuterium in the gas phase. The following experiment was performed for the purpose of ascertaining if such an interchange did occur.

A 425 cc Pyrex bulb was fitted with a three-way stopcock at the top and a stopcock at the bottom connecting with a levelling bulb. The bulb was filled with distilled water and then all but 35 cc of the water displaced by adding, through one arm of the upper stopcock, a deuterium-hydrogen mixture obtained by the electrolysis of heavy water. Both stopcocks were closed and the apparatus shaken for several minutes to saturate the water in the bulb with gas. The pressure in the bulb was about 1.1 atm. A sample of gas was then removed through the second arm of the upper stopcock, leaving the gas in the bulb at atmospheric pressure. The bulb was kept at room temperature and shaken occasionally for 19 days. At the end of this time, a second sample of gas was removed by displacement with water. Analyses of the two samples gave the results found in Table II. The first three

Table II. *Storage over water in a Pyrex vessel.*

	H_2	HD	D_2	% D
Initial sample	100	4.68	0.060	2.29
Final sample	100	4.70	0.061	2.30

columns of the table give the relative concentrations of the three molecular species based on the concentration of H_2 as 100. The last column gives the atomic percent of deuterium present in the samples.

Since these results are in disagreement with those reported by Oliphant[5] which indicate that such interchange does take place, it occurred to us that Oliphant's apparatus might have been constructed of soft glass and that possibly such an interchange might occur on a surface of soft glass but not on one of Pyrex. In order to make the test of this possibility as rigid as possible, an experiment similar to the one recorded was carried out with a bulb made of a special glass manufactured by the Corning Glass Company of Corning, N. Y., expressly for use in the construction of glass electrodes and designated by them as "Number 015." This bulb was connected with the two Pyrex stopcocks by ground joints sealed with "Picien." The total volume of the bulb and connecting tubes was 208 cc. Eighteen cc of water were left in contact with a hydrogen-deuterium mixture for 20 days. The analyses of the two samples are given in Table III. The three sets of analyses given for the first sample and the two for the last sample represent check analyses on each sample and are given to show the

[5] M. L. Oliphant, Nature **132**, 675 (1933).

TABLE III. *Storage over water in a soft-glass vessel.*

	H_2	HD	D_2	% D
Initial sample	100	43.2	7.73	19.5
	100	44.4	8.05	19.9
	100	43.5	7.82	19.5
Final sample	100	42.8	8.14	19.6
	100	44.6	8.23	20.0

experimental accuracy of the analytical method employed.

These results show definitely that the concentration of deuterium-hydrogen mixtures in contact with water remains constant if precautions are taken to avoid preferential solubility, diffusion, and the presence of metallic surfaces,[6] and that the result reported by Oliphant cannot be interpreted as being an interchange between the deuterium in the gas phase and the hydrogen atoms in the water without the aid of a catalytic surface other than the glass wall of the containing vessel.

Effect of stopcock grease

In using apparatus containing stopcocks, there was the possibility of interchange between the deuterium in the gas phase and hydrogen in the hydrocarbons contained in the stopcock grease. This possible source of error was investigated by the following experiment. Two Pyrex bulbs of approximately 50 cc capacity were evacuated and filled simultaneously from a reservoir containing a deuterium-hydrogen mixture. The first bulb was fitted with a magnetic break at the lower end and, after filling, was sealed off at the upper end. The second bulb was equipped with a stopcock and was coated on the inside with a layer of "Lubriseal." At the end of 22 days the gas in each bulb was analyzed with the results of Table IV.

TABLE IV. *Effect of stopcock grease.*

	H_2	HD	D_2	% D
Bulb I	100	4.18	0.061	2.07
Bulb II	100	4.25	0.056	2.09

It is evident, therefore, that an apparatus containing stopcocks may be used in the study of deuterium-hydrogen mixtures without fear of the occurrence of interchange between deuterium in the gas and hydrogen in the stopcock grease.

[6] J. Horiuti and Polanyi, Nature **132**, 819 (1933).

III. METHODS OF CONCENTRATION

After the discovery of the heavy isotope of hydrogen, chemists and physicists began to search for methods of concentration. It soon became evident that the two isotopes differed so greatly in properties that almost any method which was tried would give some separation but that none approached either in efficiency or in capacity that of electrolysis of water. The next, most obvious step was to study these various methods in a more quantitative way in order to elucidate the mechanisms of the processes which were operative. The purpose of this section is to treat in some detail the results obtained in the study of two such methods.

1. Diffusion through palladium

The method of diffusion through clay pipes which was used by Hertz[7] with such success in the separation of the neon isotopes has been applied by him in the preparation of spectroscopically pure deuterium in small quantities.[8] The numberless papers which have appeared on the diffusion of hydrogen through palladium at once suggested the use of a thin sheet of this metal as a diffusion membrane. While the present work was under way, a paper appeared by Harris, Jost and Pearse,[9] but, as will later be shown, their results are perhaps to be questioned.

Experimental. The first results were obtained by use of a system which had no provision for circulation of the gases. Fig. 1 is a diagram of the apparatus. The hydrogen-deuterium mixture used was obtained by electrolysis of approximately 10 percent heavy water to which sodium hydroxide had been added. *B* is a bulb of 500 cc capacity with a levelling bulb containing mercury. Oxygen was removed from the gas by passage over the platinized asbestos in *C*. The system may be evacuated through *E* which leads to a mercury diffusion pump backed by an oil pump. *F* and *M* are traps which were kept surrounded by liquid air to prevent any mercury from reaching the palladium tube, *K*, which is 5 cm long and 6 mm in diameter. A 2 cm length of

[7] G. Hertz, Naturwiss. **20**, 493 (1932).

[8] G. Hertz, Naturwiss. **21**, 884 (1933).

[9] L. Harris, W. Jost and R. W. B. Pearse, Proc. Nat. Acad. Sci. **19**, 991 (1933).

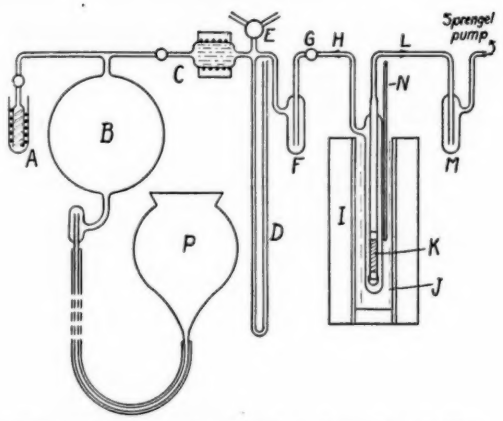

FIG. 1. Apparatus for diffusion through palladium (no circulating pump)

platinum tube of the same diameter was welded to each end of the palladium tube, and a lead glass cap fused over the lower end. Since the section of the apparatus containing the palladium tube was of soft glass, it was connected to the rest of the apparatus by the ground glass joints, *H* and *L*. In order to reduce the temperature gradient up and down the tube, the glass tube outside the palladium was wound with alternate layers of copper foil and asbestos paper, *J*. The palladium tube was maintained at the desired temperature by means of the resistance furnace *I*, the temperature being read on two calibrated thermometers (*N*) placed close to the glass tube surrounding the palladium. By raising the levelling bulb *P*, the pressure as read on manometer *D* could be kept at atmospheric until the run was nearly completed at which time the pressure was allowed to drop.

Results without circulation. Two experiments were made, three samples of gas being collected in each experiment: a sample of the original gas, the first gas that diffused through the palladium, and the residual gas remaining after nearly all of the gas had diffused through the palladium. The analyses of these samples are given in Table V.

TABLE V. *Diffusion through palladium without circulation.*

Experiment I	% D	Experiment II	% D
Initial gas	1.83	Initial gas	2.00
First 75 cc	1.56	First 62 cc	1.86
Residual 58 cc	1.81	Residual 80 cc	2.20
Total volume: 511 cc		Total volume: 519 cc	
Operating temperature: 230°C			

Circulating system. With the same palladium tube, a new apparatus was built which included a pump for circulating the gas past the palladium. The gas mixture to be diffused was introduced into the apparatus and a sample removed after the circulating pump had been allowed to operate for some time before heating up the palladium tube. As the diffusion process proceeded, the pressure in the system decreased. The final sample which was removed in each case was the residual gas left in the system and, consequently, had not diffused through the palladium.

Experimental results. Two separate runs were made using a total volume of 1350 cc of gas in each case. The analyses of the samples are given in Table VI. Operating temperature: 265°C.

TABLE VI. *Diffusion through palladium with circulation.*

		H_2	HD	D_2	% D
Exp. I	Initial gas	100	5.58	0.096	3.43
	First 52 cc	100	4.20	0.065	2.03
	Residual 69 cc	100	14.3	0.52	6.68
Exp. II	Initial gas	100	7.41	0.127	3.50
	First 35 cc	100	5.62	0.074	2.74
	Residual 65 cc	100	20.0	1.01	9.08

A third run was made using as the starting material a mixture of gas part of which was obtained by electrolysis of ordinary water and the remainder by the electrolysis of nearly pure deuterium oxide. The analyses of the samples are given in Table VII. Operating temperature: 270°C. Total volume of gas: 1350 cc. Sample *A* indicates the concentration of a sample of gas which diffused through the palladium when the pressure had dropped from 800 mm to 645 mm. Sample *B* is a similar one removed when the pressure was 136 mm. The fourth column contains the concentration of deuterium calculated as atomic percent. Column five contains the

TABLE VII. *Diffusion through palladium.*

	H_2	HD	D_2	% D	K′
Initial gas	100	32.4	43.8	34.0	0.24
First 32 cc	100	53.3	7.34	21.1	3.9
Sample *A*	100	66.2	11.5	25.1	3.8
Sample *B*	100	140.0	51.4	41.7	3.8
Final 55 cc	100	335.0	280.0	62.2	4.0

values of the concentration ratio of the reaction

$$H_2+D_2=2HD$$

as calculated by

$$K'=[HD]^2/([H_2][D_2]).$$

Discussion. The concentrations effected in the system without circulation are quite small and are of no value for any comparisons with theoretical calculations. Since the concentration effects are greatly increased by circulation of the gas, it is at once evident that a concentration gradient is rapidly set up at the surface of the palladium when no provision is made for circulating the gases, and that this gradient prevents the separation from being very efficient. These data with the static system are of practical importance in that they indicate that the frequently used method of admitting hydrogen to a hydrogen discharge tube or spectrograph through a heated palladium tube will cause no great change in the hydrogen-deuterium ratio.

The data obtained with the circulating system may be used for comparison with calculated concentration factors. As is well known, the effect of a diffusion process may be expressed by the equation

$$(Y_0/Y)=(X_0/X)^{(M_x/M_y)^{\frac{1}{2}}},$$

where X_0 and Y_0 indicate the initial and X and Y the final concentrations of the diffusing species. M_x and M_y are the corresponding molecular weights. This expression infers perfect mixing so that there is no accumulation of the less diffusible gas at the surface of the membrane. If the hydrogen and deuterium diffuse as atoms, the exponential factor in the above expression will be $2^{\frac{1}{2}}$.

The values of K' in Table VII show at once that the gas which diffuses through the palladium contains the three molecular species in about equilibrium amounts although the initial gas was not at equilibrium. The value of K' at 270°C is 3.7.[10] The value of K' for the final sample shows that equilibrium can be established on the surface of palladium without the necessity of the gas diffusing through the metal. Since this is so, no comparison can be made as to the relative rates of diffusion of HD and D_2. The only valid basis on which concentration factors can be calculated is one of atomic percent of deuterium.

The concentration factors in Table VIII are expressed as the ratio of the concentration in the final sample to the concentration in the initial gas, the concentration being expressed in atomic percent deuterium. Columns *A*, *B* and *C* refer, respectively, to the three experiments the data for which are given in Tables VI and VII. The calculated factors were obtained by the assumption that the diffusion was atomic. They are different for each experiment because of the difference in the volumes of the last samples.

TABLE VIII. *Concentration factors for palladium diffusion.*

	A	*B*	*C*
Experimental	1.95	2.59	1.84
Calculated	2.38	2.44	2.54

The experimental factors are about those to be expected from the diffusion of two species whose respective masses differ by a factor of two. Certainly the work function[11] does not have the importance assigned it by Harris, Jost and Pearse who based their conclusions on one experiment the analyses for which were obtained by the use of a Wood's discharge tube.

2. Desorption from charcoal

If hydrogen which has been adsorbed on charcoal is removed from the charcoal by evacuation, it is to be expected that the hydrogen will be desorbed more rapidly than is the deuterium. The magnitude of this difference in rates of desorption will depend upon the type of binding forces which are operative in holding the adsorbed gas to the surface. Eyring and Sherman[12] have shown that for molecules held to the surface by van der Waals forces at 90°A, the ratio of the specific desorption rates for H_2 and HD is 1.13 which is less than that due to a difference in rates of effusion. Since the porous surface of charcoal should also function as a diffusion membrane, the concentration factor might be expected to be increased by means of an effusion

[10] H. C. Urey and R. Rittenberg, J. Chem. Phys. **1**, 137 (1933).

[11] W. Jost, J. Chem. Phys. **1**, 466 (1933).

[12] H. Eyring and A. Sherman, J. Chem. Phys. **1**, 345 (1933).

process. If the gas is atomically bound to the surface of charcoal, the ratio of the specific rates of desorption of H and D will be given by the factor, $s=e^{\Delta E/RT}$, in which ΔE is the difference in the half quanta of zero point energy for an oscillator composed of a surface atom and H, and for a second oscillator composed of a surface atom and D.[12] For such a process at 90A, $s=5\times10^2$.

There are two reasons why such a process should be conducted at a low temperature. First, the amount of hydrogen adsorbed by a charcoal surface increases greatly with decreasing temperature and, since the volume of the last sample of gas removed must be of sufficient size to permit accurate analysis and, consequently, a practical limit is placed on the minimum size of this sample, the ratio of the total volume of gas used to the volume of the final sample desorbed may be increased by increasing the amount of gas initially adsorbed on the charcoal. Second, if atomic binding is operative, the factor s will be increased greatly by decrease in temperature. Whatever the type of adsorption operative in the case of hydrogen on charcoal, a selective desorption of hydrogen and deuterium is to be expected. The following experiments were carried out for the purpose of investigating this separation process experimentally.

Experimental procedure. The apparatus used is shown in Fig. 2. *B* is a liquid air trap for the purpose of precooling the gas admitted to the catalyst and also of preventing mercury from entering the catalyst bulb, *A*, in which the active charcoal was packed. The gas was admitted to the 200 cc burette *C*, measured, and then admitted to the catalyst. Before any runs were made, the charcoal was evacuated 15 hours at 400°C. All runs were made with the charcoal cooled in liquid air. After the gas had been adsorbed on the charcoal, it was desorbed by evacuation either by the Sprengel pump through *F* or by the diffusion pump through *K*. For the removal of the last portion of adsorbed gas, the charcoal was allowed to warm up to room temperature. The gas removed by the Sprengel to burette *J* could either be stored in the 500 cc bulb, *I*, or run into the sample bulb, *G*, for analysis.

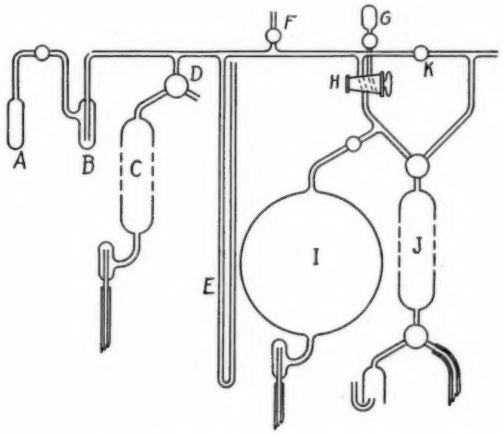

FIG. 2. Apparatus for desorption from charcoal.

Experimental results. In order to determine if concentration of the deuterium were possible by this process, two preliminary runs were made using ordinary, commercial tank hydrogen which had been purified by passage over hot platinized asbestos, calcium chloride, and phosphorus pentoxide. In the first experiment, 10.5 g of "Nuchar" No. 3, manufactured by the Industrial Chemical Company were placed in the catalyst bulb. To obtain as large a concentration as possible, the residual gas from a series of desorptions was collected in *I* until a quantity of gas was collected which was sufficient to use in a final adsorption-desorption process. Table IX gives the volume of gas adsorbed in each separate run and the volume of the last sample of gas desorbed. A period of one hour was allowed to elapse between the addition of the last hydrogen to the charcoal and the beginning of the desorption process. The pressure at the beginning of the desorption process was about 55 mm in each case. About 12 hours was required to desorb all but the last sample of gas.

TABLE IX. *Desorption from charcoal.*

Run	1	2	3	4	5	6	7	8	9	10	Total
Gas adsorbed (cc)	534	560	501	515	511	522	505	516	509	513	5715
Final sample (cc)	54	39	59	54	42	46	35	27	24	22	438

This 438 cc of gas collected in *I* was then readsorbed on the charcoal and, during the desorption process, all but the last 89 cc was discarded. Analysis of this 89 cc sample showed it to be five times as concentrated in deuterium as was the original hydrogen used.

The "Nuchar" used in the above experiment was replaced by 56.7 g of a more active cocoanut charcoal. 5085 cc of purified tank hydrogen were adsorbed on the charcoal and allowed to remain $2\frac{1}{2}$ hours before the desorption was started. The pressure was 42 mm. After 30 hours the charcoal was allowed to warm to room temperature and the last 35 cc of gas collected. Analysis of this sample showed a three-fold increase in deuterium content over that of the initial hydrogen adsorbed.[13]

For the purpose of obtaining more quantitative data on this desorption process, an experiment similar to the one above was conducted using hydrogen which had been obtained by the electrolysis of a sample of water which had been somewhat concentrated in deuterium. The data from this experiment are tabulated in Table X and plotted in Fig. 3.

TABLE X. *Desorption from charcoal.*

cc desorbed	$[HD]/[H_2]\times10^4$	$[D_2]/[H_2]\times10^4$
Initial gas	235	1.38
0–60	205	1.31
1060–1150	220	1.29
3150–3300	210	1.28
4000–4250	245	1.25
4850–4900	335	2.78
5016–5066	525	6.00

Total volume of gas : 5066 cc.
Total time of desorption : 50 hours.

Discussion. A comparison of the composition of the last sample desorbed with that of the initial gas shows the relative increase in HD concentration to be 2.23-fold and that in D_2 to be 4.35-fold. The corresponding values to be expected for a perfect diffusion process are 2.28 and 3.86, respectively. The concentration factors found experimentally are entirely too small to be ascribed to an activated adsorption and a difference in zero-point energy, but can be explained by a diffusion process combined with a van der Waals adsorption. This point will be considered at greater length in the section of this paper on the interaction of hydrogen and deuterium at surfaces.

[13] These preliminary results have been published: H. S. Taylor, A. J. Gould and W. Bleakney, Phys. Rev. **43**, 496 (1933).

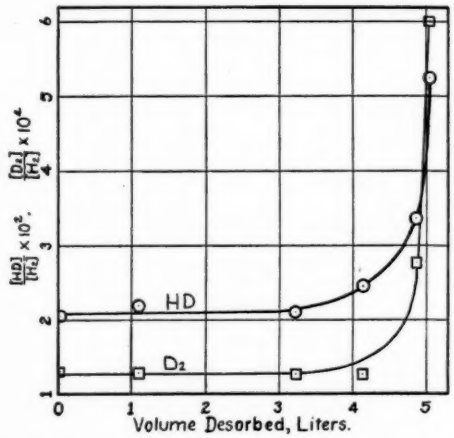

FIG. 3. Concentration of D_2 and HD by desorption from charcoal at liquid air temperatures.

Acknowledgment. The authors wish to express their thanks to Professor Edward Mack of Ohio State University, who kindly furnished the cocoanut charcoal used in these experiments.

IV. Reaction Between Hydrogen and Deuterium at Surfaces

The reaction between hydrogen and deuterium

$$H_2+D_2=2HD$$

is quite analogous in many respects to the ortho-para hydrogen conversion. A. Farkas and L. Farkas[14] report that equilibrium is established in the homogeneous gas phase above 600° which is the same sort of behavior as that found for the ortho-para conversion.[15] Urey and Rittenberg[16] have calculated the equilibrium constant

$$K=[HD]^2/([H_2][D_2])$$

for various temperatures and have checked their calculated values experimentally for higher temperatures.[16]

Until the discovery that paramagnetic surfaces which do not exhibit activated adsorption could promote the ortho-para-hydrogen conversion,[17] it

[14] A. Farkas and L. Farkas, Nature **132**, 894 (1933).
[15] A. Farkas, Zeits. f. Elektrochemie **36**, 782 (1930).
[16] H. C. Urey, R. Rittenberg and W. Bleakney, J. Chem. Phys. **2**, 48 (1934).
[17] H. S. Taylor and H. Diamond, J. Am. Chem. Soc. **55**, 2613 (1933). Emmett and Harkness, ibid. **54**, 403 (1932).

was thought[18] that a parallelism existed between the capacity of surfaces to show activated adsorption of hydrogen and their capacity to induce the spin-isomerism of hydrogen, but now that it is realized that this conversion may occur on paramagnetic surfaces on which the adsorption is exclusively of the van der Waals type, it is recognized that this conversion does not offer an unequivocal criterion of activated adsorption. If, for the case of hydrogen, activated adsorption is defined as that type of adsorption which involves linkage of the hydrogen to the surface as individual atoms, the reaction between hydrogen and deuterium does offer itself as such a criterion. Whereas the spin-isomerism of hydrogen may be effected by the presence of a magnetic field such as occurs at the surface of a paramagnetic substance or at a surface on which some paramagnetic substance such as molecular oxygen has previously been adsorbed, the reaction between hydrogen and deuterium is uninfluenced by such magnetic effects. Consequently, the reaction between hydrogen and deuterium adsorbed on a surface can result only in case the molecules lose their identity and the adsorbed hydrogen and deuterium are linked to the surface by chemical bonds. In such a case, the gas which is desorbed from the surface should be an equilibrium mixture of H_2, D_2, and HD. Accordingly, a number of surfaces have been tested as to their ability to induce this reaction.

Experimental method

The apparatus used is shown in Fig. 4. Hydrogen was prepared by electrolysis of a solution of sodium hydroxide in ordinary water and purified by passage over platinized asbestos, calcium chloride and phosphorus pentoxide. Such a preparation would contain a small quantity of HD. Deuterium was prepared by the electrolysis of deuterium oxide made conducting by allowing it to react with a little metallic sodium. The deuterium was purified by passage over platinized asbestos and through a trap cooled to $-78°$C. A given amount of each gas was admitted to the 300 cc burette, *A*, and mixed by raising and lowering the leveling bulb, which held mercury as the containing fluid. This gas mixture was

[18] H. S. Taylor and A. Sherman, Trans. Faraday Soc. **28**, 247 (1931).

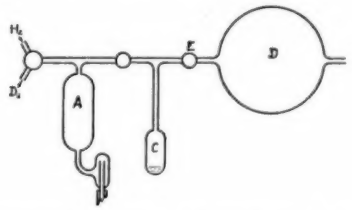

FIG. 4. Apparatus for study of reaction, $H_2+D_2=2HD$, on surfaces.

admitted to the catalyst bulb, *C*, which was 50 cc in capacity and contained in the bottom a small quantity of catalyst. After a given length of time, stopcock *E* was opened momentarily thus removing most of the gas in the gas phase from *C* into the 500 cc bulb *D* from which it was removed to the sample bulbs by means of a Sprengel pump. The catalyst bulb *C* is made with a large amount of gas space in order that the sample of gas which is removed shall not be that desorbed from the catalyst but rather that present in the gas phase. The work on charcoal has shown that such a desorption leads to separation of the isotopes.

Mercury and Pyrex surfaces

Before any trustworthy results could be obtained, it was necessary to ascertain whether any HD formation which might be detected was caused only by the catalyst under study and not at some other point in the experimental procedure.

Bradley[19] has recently found evidence of a slow activated adsorption of hydrogen on a mercury surface, and there is no *a priori* reason why the mercury present in the apparatus might not catalyze the reaction of hydrogen with deuterium. For this reason, a gas mixture was placed in the storage burette and allowed to stand for several days, samples being withdrawn at intervals and analyzed. The results are given in Table XI. This table is also of value in showing the accuracy of the analytical data. From the constancy of the values of K', the concentration ratio $[HD]^2/([H_2][D_2])$, it is apparent that neither a mercury nor a glass surface at room temperature can catalyze the reaction and that any increase in the value of K' which may be observed in subsequent experiments is attri-

[19] R. S. Bradley, J. Phys. Chem. **38**, 231 (1934).

TABLE XI. *Hydrogen and deuterium on mercury.*

Time (Days)	H_2	HD	D_2	K'
1	100	39.2	478	0.032
	100	40.5	503	0.033
2	19.3	7.4	100	0.028
	19.3	7.5	100	0.029
5	18.8	7.55	100	0.030
	19.9	7.64	100	0.029

butable in its entirety to the effect of the catalyst in C.

Chromium oxide

The chromium oxide was prepared by the method of Howard.[20] 2.58 grams were placed in the catalyst bulb and reduced for 32 hours at 340°C with tank hydrogen which had been purified by passage over platinized asbestos and through a trap cooled to −78°C. Samples of the initial gas mixture were analyzed at intervals and the concentration ratio K' found always to lie between 0.01 and 0.03. The following experimental results of Table XII are listed in the order

TABLE XII. *Reaction on chromium oxide.*

Expt.	Temp. °C	Time (hours)	Analysis H_2	HD	D_2	K'	K
1	−78	20	100	103.2	57.7	1.85	2.88
2	0	6	100	85.8	24.9	2.96	3.19
3	110	2	100	17.7	0.88	3.53	3.46
4	110	4	100	25.8	1.81	3.67	3.46
5	−78	1	100	100.5	33.8	2.99	2.88
6	−78	3	100	99.2	33.9	2.89	2.88
7	−78	15	100	99.5	32.9	3.01	2.88
8	0	1	100	95.6	28.7	3.16	3.19
9	0	3	100	102	32.2	3.23	3.19
10	−190	2	100	41.2	33.2	0.50	2.2
11	−190	26	100	73.1	22.6	2.3	2.2

in which the experiments were performed. In the last column are given the calculated equilibrium constants for the temperatures in question. From experiment 5 onwards the catalyst was evacuated for two hours at 350°C between each run. For the first four experiments the evacuation temperature was usually not so high, but no standard procedure of evacuation had been adopted.

In order to make sure that the value determined for K' at liquid air temperature is the true equilibrium value, an experiment was performed to attain equilibrium from the HD side. Since pure HD was not available a mixture with a high K' was obtained by electrolysis of a sample of heavy water. A sample of this mixture was withdrawn for analysis and the remainder admitted to the Cr_2O_3 catalyst and allowed to remain for 25 hours. The analyses are given in Table XIII.

TABLE XIII. *Equilibrium at liquid air temperature.*

Sample	H_2	HD	D_2	K'	K
Initial	100	55.7	8.67	3.57	
Final	100	40.2	7.39	2.18	2.2

Nickel

Approximately 1.8 g of a NiO-kieselguhr preparation was placed in the catalyst bulb. With purified tank hydrogen flowing through the apparatus, the catalyst was warmed slowly to 500°C and kept at that temperature for 90 minutes. After evacuation overnight at 430°C, experiments similar to those for Cr_2O_3 were performed. The experimental results in Table XIV were obtained. A different catalyst was

TABLE XIV. *Reaction on nickel.*

Expt.	Temp. °C	Time (hours)	Analyses H_2	HD	D_2	K'	K
1	−190	2	100	80.2	543	0.12	2.2
2	−190	4	100	58.5	529	0.07	2.2
3	−190	48	100	65.5	553	0.08	2.2
4	−78	19	100	83.0	24.6	2.80	2.88
5	0	6	100	64.4	12.3	3.37	3.19
6	110	2	100	67.1	17.4	2.58	3.46
7	−190	21	100	77.5	44.5	1.34	2.2
8	0	15	100	108.1	36.5	3.19	3.19
9	110	2	100	114.5	37.7	3.47	3.46
10	110	4	100	114.8	38	3.45	3.46

used in the first six experiments than was used in the last four. A standard evacuation technique of 2 hours at 430°C was adopted.

In order to approach equilibrium at −78°C from the other side, a mixture showing a high K' was placed on the catalyst for 19 hours and the data of Table XV was obtained.

[20] J. Howard, Princeton Thesis, 1933. Trans. Faraday Soc. **30**, 278 (1934). See also, Lazier and Vaughen, J. Am. Chem. Soc. **54**, 3080 (1932).

TABLE XV. *Equilibrium at −78°C.*

Sample	H_2	HD	D_2	K'	K
Initial	100	63.0	11.2	3.57	
Final	100	54.5	10.2	2.89	2.88

Wet soft-glass surface

The data given in Table III may be used to show that the value of the equilibrium constant remains unchanged after the gas has been in contact with a moist, soft-glass surface for a period of 20 days. The values of K' calculated from these data are given in Table XVI.

TABLE XVI. *Hydrogen and deuterium on moist soft-glass.*

	K'		
	1	2	3
Initial sample	2.40	2.43	2.41
Final sample	2.25	2.40	

Columns 1, 2, and 3 represent check analyses on the same sample of gas. The calculated value of K at room temperature is 3.25. If, therefore, a moist, soft-glass surface were efficacious in promoting this reaction, the values of K' determined for the final sample should be higher than those for the initial sample. Such is not the case.

Charcoal at liquid air temperature

Bonhoeffer and Harteck[21] showed that charcoal at liquid air temperatures is very efficient in converting ortho- to para-hydrogen. Taylor and Sherman[18] and, later, Bonhoeffer, Farkas and Rummel[22] showed that the conversion efficiency decreased with increasing temperature until the efficiency dropped to zero at room temperature, but that at higher temperatures the efficiency began to increase with increasing temperature. The latter authors interpreted the high temperature conversion as being due to an activated adsorption and the low temperature conversion as being due to a van der Waals adsorption plus a magnetic effect either of the charcoal surface itself or of impurities in the charcoal. In view of the previously quoted work on paramagnetic surfaces,[17] such an interpretation of the low temperature work seemed logical, but direct proof was lacking.

[21] Bonhoeffer and Harteck, Zeits. f. physik. Chemie **B4**, 113 (1929).

[22] Bonhoeffer, Farkas and Rummel, Zeits. f. physik. Chemie **21B**, 225 (1933).

The data of Table X offer two arguments in favor of such a conclusion. If these data are used in the calculation of K', the values in Table XVII are obtained. If the hydrogen were held to the surface atomically, equilibrium between the molecular species (H_2, D_2 and HD) should be attained and the values of K' in the above table should approach the calculated value for K of 2.2 for this temperature. Instead, they remain high. Moreover, if activated adsorption were present but the establishment of equilibrium were a slow process, the last values of K' should be lower than the first since these last samples had been on the charcoal some two days. On the contrary, they become larger due to the more rapid desorption of H_2. It should be added that Farkas and Farkas[14] report no HD formation on charcoal at −195°C.

TABLE XVII. *Equilibrium constants on charcoal.*

cc desorbed:	Initial gas	0–60	1060–1150	3150–3300
K':	4.0	3.2	3.8	3.5
cc desorbed:	Initial gas	4000–4250	4850–4900	5016–5066
K':	4.0	4.8	4.0	4.6

The concentration factors obtained are also explicable only in terms of a van der Waals adsorption. Whereas an activated adsorption would necessitate a ratio of rate of desorption of hydrogen to rate of desorption of deuterium of $s=500$,[12] the concentration observed corresponds almost exactly to that attainable from a diffusion process for which the ratio of specific rates is given by the expression

$$s=(M_2/M_1)^{\frac{1}{2}},$$

M_1 and M_2 being the molecular weights of the diffusing species. For H_2 and HD, $s=1.15$. For H_2 and D_2, $s=1.41$.

The results show decisively that the adsorption of hydrogen on charcoal at the temperature of liquid air is of the van der Waals type and that the ortho-para conversion observed under these conditions is due solely to the paramagnetism of the surface.

Palladium

The data given in Table VII may be used for an investigation into the effect of palladium in

promoting the reaction between hydrogen and deuterium. The values of K' are obtained. (Table XVIII.) The calculated value of K at 270°C is 3.67.

TABLE XVIII.

Sample.	Initial gas	First 32 cc	A	B	Final
K':	0.24	3.87	3.85	3.81	4.00

Discussion

If the first four experiments on Cr_2O_3 are considered only as preliminary work, the data show that reaction between hydrogen and deuterium occurs on the surface of Cr_2O_3 in the temperature range between −190 and 110°C and that the rate of this reaction is rapid. At −190° the value of K' rises from 0.03 or less initially to 0.5 in two hours and equilibrium is attained in 26 hours. At −78° the rate has become so rapid that equilibrium is attained in one hour. On the assumption that activated adsorption is a necessary prelude to chemical reaction at surfaces, the adsorption of hydrogen on Cr_2O_3 even at these low temperatures must be partly of the activated type. In view of the work of Howard,[20] who measured both van der Waals and activated adsorption on chromium oxide, the existence of an activated adsorption below 0°C was very surprising.

Since equilibrium is established in the gas phase, the rate of adsorption and desorption must be rapid and, since this process proceeds rapidly at low temperatures, the desorption process must have a low activation energy of the order of a few kg cal. and, consequently, the heat of adsorption must be yet smaller. Howard found the high temperature adsorption process to have a heat of adsorption of ~25 kg cal. and an activation energy of ~20 kg cal. Since any desorption process requiring an activation energy of 45 kg cal. will proceed at an immeasurably slow rate at low temperatures, it is obvious that the activated adsorption which is operative at low temperatures has entirely different characteristics from that measured by adsorption measurements at high temperatures.

That the adsorption is of the activated type may be easily seen. Any acceleration in rate of reaction caused by a van der Waals adsorption can only be due to an increase in the concentration of the reactants at the surface, and such a concentration cannot cause the rapid reaction of hydrogen and deuterium. Experimentally, this fact is known from the work on charcoal which shows that at −190°C where the adsorption is large, there is no reaction.

With nickel, the results are almost the same as with Cr_2O_3 except that the catalyst is not so active and reaction at −190°C is slower than it is with Cr_2O_3. With Cr_2O_3 at that temperature equilibrium is attained in 26 hours, but with nickel the value rises only to 1.34 in 21 hours. Analogous energy considerations hold in the two cases; the activated adsorption which is observed at low temperatures must have different characteristics from that measured by Benton and White.[23]

No claim is made that all of the low temperature adsorption on Cr_2O_3 and Ni is of the activated type. Any surface which will promote the reaction of hydrogen and deuterium will also promote the ortho-para hydrogen conversion, but, because of magnetic effects, the converse is not true. In a flow system at liquid air temperatures Cr_2O_3 gives 100 percent conversion of

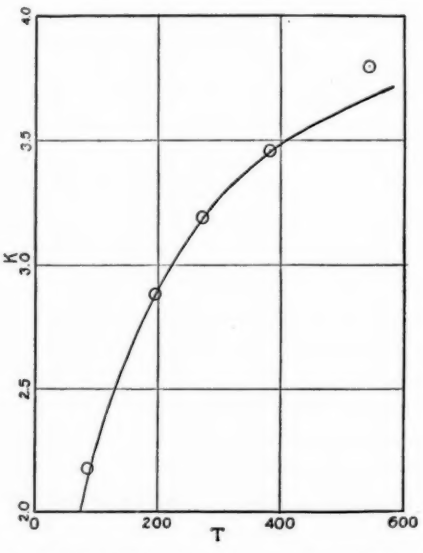

FIG. 5. Variation with temperature of the equilibrium constant for the reaction between hydrogen and deuterium.

[23] A. F. Benton and T. A. White, J. Am. Chem. Soc. 52, 2325 (1930).

ortho- to para-hydrogen at a space velocity of 60, while the results here recorded show that the hydrogen-deuterium reaction is comparatively much slower. It is evident, therefore, that the effect of the activated adsorption at this temperature on the ortho-para conversion is negligible as compared with the combined effect of van der Waals adsorption plus the paramagnetism of the surface. The reaction between hydrogen and deuterium does offer a method for the detection of activated adsorption in temperature regions in which it would be indistinguishable from van der Waals adsorption by the experimental methods customarily employed.

These results show that some of the hydrogen adsorbed on Cr_2O_3, Ni and undoubtedly other catalytic surfaces is in a chemically very reactive form even at liquid air temperatures and that, consequently, the reaction kinetics of a catalytic hydrogenation process is determined rather by the behavior of the substance hydrogenated than by the hydrogen.

Finally, the data give an experimental determination of the variation of the equilibrium constant, K, as a function of temperature from -190 to 270°C. The data are plotted in Fig. 5. The curve is that calculated from statistical mechanics by Urey and Rittenberg and the points represent values obtained in this investigation.

The Mercury Photosensitized Decomposition of the Deuteroammonias

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A method of preparation of ammonias in which one, two and three hydrogens are replaced by deuterium has been devised. It reveals that the preparation of magnesium nitride from magnesium and ammonia yields amido- or imido-compounds as intermediate stages of great stability. The physical properties of deuteroammonia preparations have been studied. Ultraviolet absorption spectra reveal the presence of all three substituted deuteroammonias in the preparations studied. The mercury photosensitized decomposition of trideuteroammonia is more than ten times slower than the corresponding reaction of ammonia. It is also inhibited much more strongly by deuterium than is ammonia decomposition by hydrogen. Increasing deuterium content of ammonia decreases the rate of sensitized decomposition. The kinetics of decomposition are qualitatively similar but quantitatively different. The quantitative results are compared with data on quenching of fluorescence of mercury resonance radiation by the several gases in question and lead to important conclusions concerning the nature of the collisions involved in the decomposition process.

THE isolation of deuterium oxide from water by processes of electrolytic separation offers the experimental chemist a large field of investigation into compounds in which deuterium has displaced hydrogen. It is evident that the choice of compounds to be studied is very large and choice will at first be best dictated by the use to which the products may be put in testing various physico-chemical theories. It is for reasons of this kind that we have prepared derivatives of ammonia and obtained products which contain ammonias in which one, two and three atoms of hydrogen have been replaced by deuterium. We shall show that this work has led to interesting conclusions concerning the preparation of magnesium nitride, to important observations concerning the physical properties of the ammonias, to measurements of the absorption spectra of the ammonias for ultraviolet light and to a determination of the relative stabilities of the several ammonias towards collisions with excited mercury.

PREPARATION OF THE DEUTEROAMMONIAS

Three different preparations of the deuteroammonias have been made by allowing the vapor of deuterium oxide ($D_4^{20} = 1.1052$) to interact with three different preparations of magnesium nitride. The vapor was allowed to diffuse into an evacuated tube containing the

[1] C. R. B. Fellow from Louvain University, 1933–1934.

magnesium preparation at room temperatures. Ready reaction occurred with evolution of heat, the resulting ammonia being pumped off and condensed in a trap cooled in liquid air. To ensure complete reaction of the water vapor the gas was passed backwards and forwards several times over the magnesium preparation which was finally heated during evacuation to remove any adsorbed gas. Specific gravity determinations by the ordinary gas density method of the dried and redistilled products showed that their densities, relative to that of ordinary ammonia, indicated them to contain 68, 90 and >99 percent of their hydrogen content as the deuterium isotope.

These differences in deuterium content are to be ascribed to the magnesium nitride preparations used. The 68 percent material was prepared from a product obtained by passing dry ammonia over heated magnesium filings. Prior to use it was subjected to evacuation with a good pumping system at ordinary temperatures. The second preparation leading to the 90 percent D product was from a similar magnesium preparation which was however evacuated for 40 hours at 400°C. It is quite evident that such methods of preparation do not yield pure Mg_3N_2 but material in which, depending on the degree of evacuation, greater or lesser amounts of hydrogen remain bound as amido- or imido-groups. This hydrogen would escape the normal analytical methods of identification, but the interaction with deuterium oxide at once exhibits its presence in such preparations. Similar observations as to intermediate stages of decomposition have been made by Frankenburger and Hodler,[2] by other methods in the case of tungsten powder. For the preparation containing >99 percent of the hydrogen in the form of the D isotope, the magnesium nitride was prepared by the interaction of magnesium filings and purified nitrogen.

Physical Properties of the Deuteroammonias

The specific gravities ($NH_3=1$), freezing points and boiling points of ammonia and of the three preparations are exhibited in Table I.

Table I.

Percentage of Deuterium	0	68	90	99
Specific Gravity ($NH_3=1$)	1	1.12	1.158	1.174
Freezing Point, °Abs.	195.2	197.9	198.6	199
Boiling Point, °Abs.	239.75	241.7	242.1	242.3

By means of a differential tensimeter, using ammonia as reference, the vapor pressure data of Table II were obtained for the >99 percent ND_3 product.

Table II.

T°Abs.	202.3	213	226.1	232.1	238.6
P_{NH_3}	77	184	364	511	714
P_{ND_3}	63	154	313	445	628

Assuming the latent heat of vaporization of ammonia to be 5797 cal. per mole at 1 atmosphere, the vapor pressure curve of the product gives a value for the latent heat of vaporization of ND_3 of 5990 cal. per mole.

Absorption Spectra of the Deuteroammonias

In Fig. 1 are shown spectrophotometric curves of the ultraviolet absorption of ordinary ammonia and the product containing 68 percent of the heavy isotope. In Fig. 2 similar curves are given for the 68 and 90 percent products. The figures also show the copper arc spectrum for reference purposes and the curves have been lined up therewith with respect to one another.

It is at once evident that the substitution of the heavy isotope has brought about a displacement of the absorption bands to shorter wavelengths. The more complex structure in the principal band of the 68 percent product has been analyzed by Dr. W. S. Benedict who ascribes the structure to the presence of the three deuteroammonia molecules NH_2D, NHD_2 and ND_3, the displacement to shorter wavelengths being progressively greater with increased substitution in the ammonia molecule. On the laws of chance a product containing 68 percent D should contain approximately 34 percent ND_3, 44 percent ND_2H, 19 percent NDH_2 and 3 percent NH_3. A 90 percent D sample should contain on the same basis only 25 percent ND_2H, 3 percent NDH_2 and negligible amounts of NH_3. It will be seen from a comparison of Figs. 1 and 2 that the spectrophotometric

[2] Frankenburger and Hodler, Trans. Faraday Soc. **28**, 229 (1932).

curves of the absorption bands are in fair agreement with this calculation and that we have in the ultraviolet absorption spectra a convenient semi-quantitative method of identification of the three deuteroammonias.

These spectra were made with the ammonias at room temperature and 40 mm pressure in quartz vessels 30 mm long. A more penetrating study of these absorptions at other pressures and temperatures is in progress.

The Mercury Photosensitized Decomposition of the Deuteroammonias

To compare the photochemical stabilities of the deuteroammonias relative to that of ammonia, their decomposition under the influence of excited mercury was studied. The characteristics of the ammonia decomposition under such conditions are already well known.[3, 4, 5]

Apparatus

The measurements were carried out in an apparatus an outline of which is shown in Fig. 3. The gas to be studied was withdrawn from the reservoir *A* through the tube *B* to the quartz reaction vessel *D*. During illumination the

[3] Dickinson and Mitchell, J. Am. Chem. Soc. **49**, 1487 (1927).

[4] Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

[5] Melville, Proc. Roy. Soc. **A138**, 384 (1932); Trans. Faraday Soc. **28**, 805 (1932).

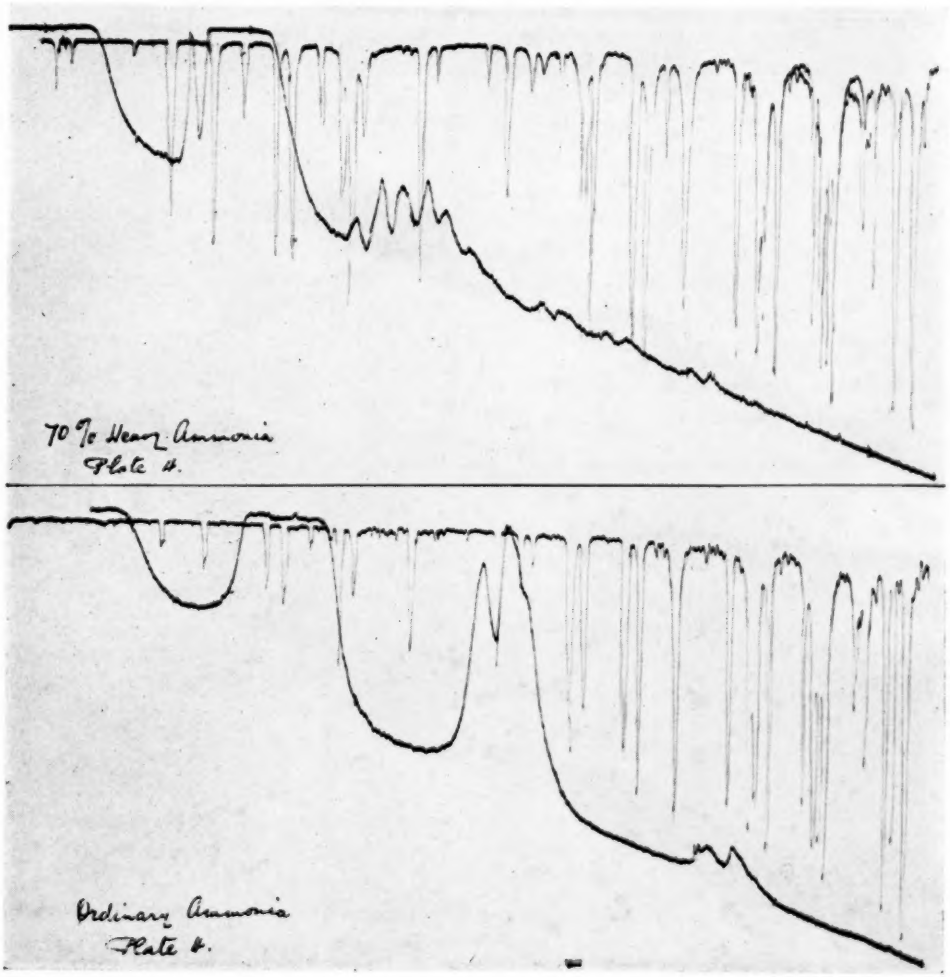

FIG. 1. Ultraviolet absorption spectra of ammonia and deuteroammonia (=68 percent ND_3).

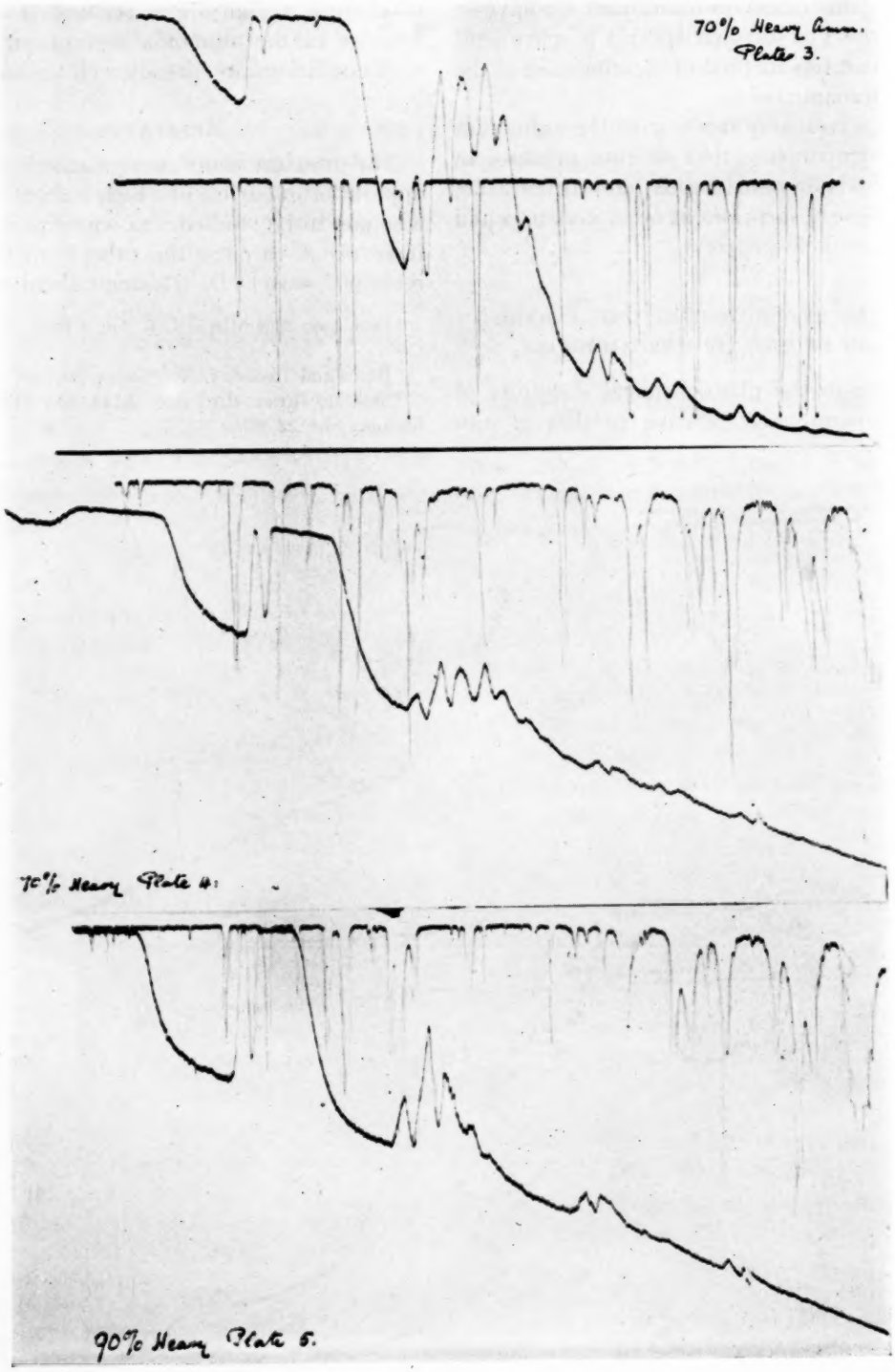

FIG. 2. Ultraviolet absorption spectra of deuteroammonias (=68 and 90 percent ND_3).

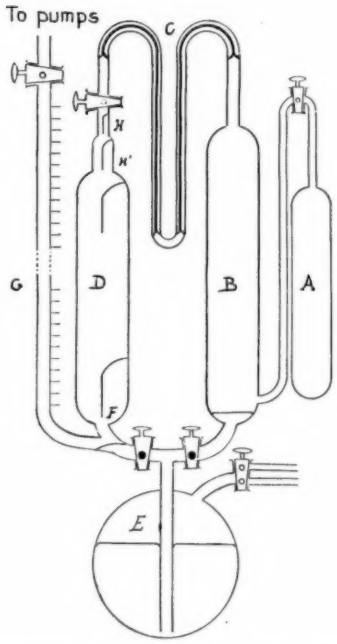

FIG. 3. Apparatus for photosensitized decomposition of ammonias.

mercury from the reservoir E was raised in B as far as the capillary U-tube, C. The pressure of gas in the quartz vessel was measured by means of the manometer G with the mercury level in D at the lowest pointer level F. The rate of decomposition was ascertained after a given period of illumination by condensing the ammonia in the U-tube C with the aid of liquid air, reading off the pressure of residual gas so produced on the manometer G, the sensitivity of the measurement being increased by raising the mercury level in D to the upper pointer level H. After this pressure measurement, the condensed gas was again vaporized, mixed by alternately raising and lowering the mercury levels in B and D and brought back for re-illumination to the quartz vessel as in the initial stages.

LIGHT SOURCE

As source of resonance radiation use was made of the new Hanovia quartz mercury vapor rare gas discharge tube, Sc-2537, developed initially for Raman effect determinations. The discharge tube used was a double-U grid type operating at 5000 volts delivered from the 110 volt a.c. lighting circuit through a 30 milliampere transformer. The advantage of this type of tube is that 85 percent of the generated light is in the band at 2537A and the resonance line is non-reversed. The tube operates at little above room temperatures. With a 20 inch tube consuming 25 watts as much as 40 micro-watts of non-reversed radiation ($\lambda = 2537$A) per square centimeter is obtained at 20°C. This is as great an intensity of light of this wave-length as is obtained from the d.c. Alpine Sun Lamp consuming 300 watts. The Sc-2537 type lamp is the most convenient source of mercury resonance radiation that we have thus far employed. The intensity of the light is constant and reproducible over many hours of illumination. Some diminution in light intensity results after the tube has been used during some hundreds of hours, due to the well-known deterioration of quartz in the presence of excited mercury atoms. Our experience in this research is paralleled by that of others in the laboratory with two other arcs of this type, one a 30, the other a 100 milliampere tube.

The light used was filtered through a layer, 1.5 cm thick of 25 percent acetic acid solution in a quartz vessel. This eliminates the light in the region of 2000–2300 to which the gases are photochemically sensitive.

COMPARATIVE RATES OF DECOMPOSITION OF NH_3 AND ND_3

The data in Table III show that the pure deuteroammonia is much less sensitive to photosensitized decomposition than is ordinary ammonia. The experiments were done under strictly comparable conditions at the same initial pressure of the two gases.

TABLE III. *Photosensitized decomposition of NH_3 and ND_3, initial gas pressure, 48.7 mm.*

Gas	Time of illumination (min.)	Total press. of non-condensible gas (mm)	ΔP (mm)	$1/R$ (min./mm)	$1/R_0$ (min./mm)	$\bar{P}_{(H_2 \text{ or } D_2)}$ (mm)	$P_{(H_2 \text{ or } D_2)_i}$
NH_3	10	0.225	0.225	44.4		0.084	
	20	0.561	0.336	59.5	38.4	0.295	0.520
	20	0.831	0.270	74.0		0.522	
ND_3	30	0.057	0.057	522		0.019	
	60	0.132	0.075	806	410	0.071	0.072
	60	0.190	0.058	1022		0.121	

The successive intervals of illumination are shown in the second column. The cumulative residual gas pressure in mm resulting from the decomposition is shown in the third column, the increase in this pressure in mm for the given time interval is shown in the fourth column. In the fifth and seventh columns are shown the reciprocal rates of reaction and the mean hydrogen pressures during the period of illumination. The sixth column records the reciprocal of the initial rate of decomposition, $1/R_0$, for $P_{H_2}=0$ obtained by plotting the observed reciprocal rates against the mean $\overline{P}_{H_2}$ for the interval and extrapolating the straight line joining the points to zero P_{H_2}. The final column shows the calculated hydrogen pressure at which the rate of reaction is reduced to one-half the initial rate of reaction, R_0.

From these typical data it can be concluded that the ND_3 molecules are $410/38.4=10.7$ times less reactive than the NH_3 molecules under the given conditions of concentration and illumination. In each case, the reciprocal rate of reaction is directly proportional to the mean hydrogen (or deuterium) pressure. This confirms the previous finding of Dickinson and Mitchell for NH_3. The ND_3 decomposition is, however, much more pronouncedly affected by deuterium pressure than is NH_3 by hydrogen. A deuterium pressure of 0.072 mm reduces the initial rate of ND_3 decomposition to half value whereas a hydrogen pressure of 0.52 mm is required for the NH_3. This represents a ratio, $52:7.2=7.2:1$.

Influence of Concentration of Deuterium in the Ammonia Molecule

The velocities of decomposition of the four ammonias, NH_3, and samples containing 68, 90 and >99 percent of the hydrogen as D, were illuminated under comparable conditions of light intensity at mean pressures of 40 mm. Table IV shows that the decomposition produced in (a) 30 minutes illumination and (b) 15 minutes illumination decreases progressively as the deuterium content increases. The two series are not comparable one with another since the light intensities differed in the two series.

Table IV. *Influence of deuterium content on rate.*

Percentage of hydrogen as deuterium		0	68	90	>99
Rate of decomposition in mm$\times 10^{-3}$/min.	(a)	16.9	3.83	2.23	1.6
	(b)	51.1	11.45	7.0	5.0

Influence of the Pressure of Deuteroammonia

The velocity of photosensitized decomposition was studied under constant conditions of illumination, temperature and mercury pressure at pressures of deuteroammonia equal to 40.5, 21.3, 11.0 and 4.9 mm Hg. The deuteroammonia used had a velocity of decomposition relative to that of ammonia corresponding to a preparation containing 80 percent of the hydrogen present in the form of deuterium. The experimental data are presented in Table V in which the columns have the same significance as those of Table III.

Under the same experimental conditions the data of Table VI are typical of those obtained with ammonia.

The values for $1/R_0$ thus obtained, when plotted against the reciprocal of the deuterammonia pressure, give a straight line. This result which was previously found by Mitchell and Dickinson for ammonia is also true of our ammonia preparation at the pressures used in these studies. The variation in $1/R_0$ is, however, much smaller with ammonia than with deuteroam-

Table V. *Influence of pressure on reaction rate.*

Deutero-ammonia press. (mm)	Time of illumination (min.)	Press. of non-condensible gas (mm)	ΔP (mm)	$1/R$ (min./mm)	$1/R_0$ (min./mm)	$\overline{P}_{(D_2)}$ (mm)	$P_{(D_2)\frac{1}{2}}$ (mm)
40.4	15	0.189	0.189	79		0.094	
	31	0.365	0.176	176	34	0.277	0.060
	62	0.594	0.229	271		0.480	
21.3	15	0.108	0.108	138		0.054	
	30	0.205	0.097	311	44.5	0.156	0.028
	60	0.326	0.121	500		0.269	
11.0	15.5	0.069	0.069	224		0.035	
	32	0.130	0.061	526	67	0.100	0.014
	45.5	0.190	0.060	758		0.160	
4.9	15	0.042	0.042	358		0.021	
	30	0.080	0.038	794	125	0.061	0.011
	45.5	0.119	0.039	1158		0.099	

TABLE VI.

Ammonia press. (mm)	Time of illumination (min.)	Press. of non-condensible gas (mm)	ΔP (mm)	$1/R$ (min./mm)	$1/R_0$ (min./mm)	$P_{(H_2)}$ (mm)	$P_{(H_2)_{\frac{1}{2}}}$ (mm)
42.2	5	0.400	0.400	12.5		0.150	
	10	0.895	0.495	20.2	9.0	0.486	0.385
	15	1.409	0.514	29.2		0.864	
10.8	5	0.171	0.171	29.2		0.064	
	10	0.334	0.163	61.3	12.0	0.190	0.045
	15	0.493	0.159	94.3		0.310	

monia. For ammonia pressures of 10 and 40 mm Hg we find values for $1/R_0$ of 12 and 9 min./mm, respectively, as contrasted with 67 and 34 min./mm for the 80 percent deuteroammonia studied. With both types of ammonia, however, it is evident that the rate of sensitized decomposition increases with increasing ammonia pressure, the conditions of mercury sensitization being maintained constant.

THE KINETICS OF THE DECOMPOSITION PROCESS

The experimental data indicate that the kinetic expression must account for similar effects in the cases of both ammonia and deuteroammonia. The rate of sensitized decomposition increases with initial gas concentration and is inhibited by the hydrogen or deuterium produced. The kinetic picture should account for the quantitative differences in reaction rates, for the more pronounced influence of the deuterium on the decomposition of deuteroammonia than of hydrogen on ammonia, and also for the greater variation in initial rate of decomposition with change in initial deuteroammonia pressure.

Mitchell and Dickinson and Melville derived kinetic expressions both of which led to an equation of the same form for the initial rate of reaction in absence of hydrogen. Melville's approach was the simplest. He assumed that collision with excited mercury led to decomposition,

$$R=-d[NH_3]/dt=k_1[Hg'][NH_3]. \quad (1)$$

He derived the concentration [Hg'] from a stationary state equation,

$$d[Hg']/dt=K-k_1[Hg'][NH_3]-k_2[Hg'][H_2]-k_3[Hg']=0,$$

where K is proportional to the intensity of illumination and the mercury vapor concentration and the third and last terms take into account deactivation by collision with H_2 (k_2) and by radiation of resonance radiation (k_3). The rate then becomes

$$R=\frac{Kk_1[NH_3]}{k_1[NH_3]+k_2[H_2]+k_3} \quad (2)$$

or

$$\frac{1}{R}=\frac{1}{K}\left(1+\frac{k_2[H_2]+k_3}{k_1[NH_3]}\right), \quad (3)$$

whence

$$\frac{1}{R_0}=\frac{1}{K}\left(1+\frac{k_3}{k_1[NH_3]}\right). \quad (4)$$

These equations conform with the experimental observations that $1/R$ plotted against $p_{H_2 \text{ or } D_2}$ for constant $[NH_3]$ or $[ND_3]$ gives a straight line and that $1/R_0$ plotted against $1/[NH_3]$ is also a straight line. The equation may be used to express the initial rate R_0 and the rate R_H at a given hydrogen (or deuterium) concentration $[H_2]$ or $[D_2]$ in the form,

$$(R_0-R_H)/R_H=k_2[H_2]/(k_1[NH_3]+k_3). \quad (5)$$

If $[H_2]_{\frac{1}{2}}$ or $[D_2]_{\frac{1}{2}}$ is the hydrogen or deuterium concentration necessary to reduce R to $\frac{1}{2}R_0$ it follows that

$$k_2[H_2 \text{ or } D_2]_{\frac{1}{2}}=k_1[NH_3 \text{ or } ND_3]+k_3. \quad (6)$$

All our experimental data are in qualitative agreement with these kinetic equations but a quantitative correlation fails. We ascribe this in part to the experimental conditions of pressure under which we were forced to operate with the deuteroammonias owing to their low reactivity. These high gas pressures effect a broadening of the resonance line which prevents the exact application of the usual principles governing energy exchange between excited atom and colliding molecule.

Comparing ammonia and 80 percent deuteroammonia we find by application of Eq. (4) that the ratio k_1/k_3 obtained from the ratio of the intercept to the slope of the plot of $1/R_0$ against $1/[NH_3]$ gives the two values of 0.19 and 0.045 mm^{-1}, respectively. From these one deduces a ratio of $k_{1_{NH_3}} : k_{1_{(80 \text{ percent } ND_3)}} = 4.2 : 1$. On the other hand, from Eq. (6) with the data in

Tables V and VI we get values for $k_1/k_2=0.011$ for ammonia and 0.0016 for the 80 percent deuteroammonia. We are compelled to assume that k_2 is the same for both hydrogen and deuterium, since Dr. M. G. Evans has found that these gases have exactly the same effect in extinguishing the fluorescence of excited mercury. Hence we conclude that, calculated in this manner, $k_{1_{NH_3}} : k_{1_{(80\ \text{percent}\ HN_3)}}=0.001 : 0.0016$ or approximately 7 : 1. When we compare the value for $k_1 : k_2=0.011$ for ammonia with that found by Melville from the data of Mitchell and Dickinson, namely 0.028, we can see that the ratio is dependent to some extent on the experimental conditions.

Whatever the actual magnitudes of k_1 for ammonia and deuteroammonia may be, it is clear that k_1 for the ammonia reaction is several times that for the deuteroammonia decomposition. It follows, therefore, from Eq. (6), that the inhibitory action of deuterium, since it has a quenching efficiency equal to that of hydrogen, must be more pronounced in the case of deuteroammonia than with ammonia. Tables III, V and VI show this quite effectively. Melville has already emphasized the same point in comparing the influence of hydrogen on the sensitized decomposition of ammonia and on the much faster reaction of excited mercury with phosphine. Similarly the relative values of k_1 account for the greater variation of $1/R_0$ for the deuteroammonia reaction with change in initial pressure.

We desire to call attention to the fact that our ratios for $k_1 : k_2$, 0.011 for ammonia and 0.0016 for deuteroammonia are very much less than the values that one derives for these quantities on the assumption that the efficiencies of quenching of resonance fluorescence are a measure of these quantities. Dr. Evans will record elsewhere the details of these measurements, which give him, for the quenching ratios, the values 0.18 for hydrogen and ammonia and 0.06 for deuterium and deuteroammonia. The hydrogen-ammonia quenching ratio is several fold greater even than the value of 0.028 cited above for $k_1 : k_2$. Also the quenching ratio of ammonia and deuteroammonia is 3 : 1 as compared with the values of 4.2 and 7 : 1 obtained in the preceding calculations. We believe that this should be taken to indicate quite decisively that only a small fraction of the collisions with ammonia or deuteroammonia which are efficient for quenching of fluorescence lead to decomposition of the molecule. From the values of the intercepts in the plots of $1/R_0$ against $1/[NH_3]$ and $1/[ND_3]$ we believe that the probability of a molecule decomposing on collision is at least twice as great with NH_3 as with ND_3. We conclude, therefore, that the bulk of the quenching by these gases must be ascribed to collisions involving the transfer of the excited mercury atom from the $^3P_1$ to the $^3P_0$ state. The energy thus accumulated by the ammonias, 0.218 volt, is quite inadequate to produce ammonia decomposition on subsequent collisions. We can assert this with confidence from our knowledge of the absence of homogeneous thermal decomposition of ammonia even at quite high temperatures. With Dr. Evans, we have made several attempts to amplify the theoretical approach to the kinetics of the problem on this basis. While we have been able thus to remove some of the difficulties in the simpler treatment of Melville employed above, we have not been able to bring all the experimental facts quantitatively within the framework of a theory. We are planning further photochemical studies of deuteroammonia which may assist in a final satisfactory solution. In the meantime we wish to express our indebtedness to Dr. Evans for his assistance in these attempts as well as for his courtesy in placing his data on quenching of resonance fluorescence immediately at our disposal.

Acid-Base Reactions Involving Deuterium

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From measurements of the rate of neutralisation of a pseudo-acid, nitroethane, in heavy water, a comparison is made of the relative rates of ionisation of protium and deuterium atoms, the ratio being approximately 10 : 1. It is shown that these relative rates are of great importance in the study of catalysis by acids and bases in heavy water and some conclusions may be drawn with regard to the mechanism of the inversion of sucrose and of the mutarotation of glucose. These results also have a bearing on the question of deuterium-protium exchange in compounds when dissolved in water.

THE work of Brönsted[1] and others has established the general nature of acid-base equilibria and the application of these ideas to catalytic reactions has effectively settled the main problems of acid and basic catalysis. The discovery of deuterium, the hydrogen isotope of mass 2, however, has made it necessary to examine how far the previous ideas may be applicable to compounds containing this isotope and at the same time has provided a valuable tool for probing further into the nature of various reactions.

From the standpoint of acids and bases it is interesting to compare the strength of proto- and deuto-compounds but for such a comparison a mere determination of dissociation constants will not suffice, since the equilibria involved are different in the two cases; thus an acid HA ionises in ordinary water according to the scheme

$$HA+H_2O\rightleftharpoons OH_3^++A^-,$$

whereas the corresponding deuto-acid will ionise in heavy water according to the scheme

$$DA+D_2O\rightleftharpoons OD_3^++A^-.$$

These two equilibria are affected by the dielectric constants of the solvents, the degree of hydration of the ions and neutral molecules as well as by the relative affinities of the anions and water molecules for protons and deutons. It is, therefore, evident that no simple conclusion with regard to the strength of any particular bond between atoms can be drawn from the data.* Although equilibrium data will fail to give direct information of the relative strengths of proto- and deuto-acids, it should be possible to make such a comparison from the rates at which the compounds lose protons and deutons, respectively. For many chemical reactions as well as biological processes these relative rates will be of much greater significance than the dissociation constants, which in themselves can only be applicable to other equilibria such as are involved in studies of partition between phases, solubility and indicator reactions. The correspondence between acid strength and catalytic activity which is expressed in the generalised theory of acid and basic catalysis is a consequence of the relation between acid strength and the rate of proton transfer. If a deuto-acid is compared with a proto-acid this relation will almost certainly break down and, consequently, in this most characteristic property of acids—their ability to facilitate prototropic reactions—there can be no comparison of the two types of compound through their dissociation constants. It also follows that any attempt to formulate a "pD" scale for heavy water on the same basis as the pH scale for ordinary water will be quite misleading, except for equilibria, unless the different velocities of ionisation of deuterium and protium are taken into account.

In order to compare the rates at which protons and deutons are transferred between molecules, it was decided to study the neutralisation of a pseudo-acid in heavy water. The phenomenon of the slow neutralisation of pseudo-acids was interpreted by Hantzsch[2] as a slow rearrange-

[1] Brönsted, see Chem. Rev. **5**, 231 (1928).

* The contrary conclusion of Lewis and Schutz (J. Am. Chem. Soc. **56**, 1002 (1934)) is based on a misunderstanding of the nature of acid dissociation.

[2] Hantzsch, Berichte **32**, 575 (1899).

ment of the pseudo-acid into a genuine acid which is instantaneously neutralised. Thus for nitromethane Hantzsch would write

$$CH_3NO_2 \xrightarrow{slow} CH_2 : NOOH$$

$$+OH^- \xrightarrow{inst.} CH_2 : NO_2^- + H_2O.$$

Recently Pedersen[3] has shown that the isomerisation of nitromethane is a base catalysed reaction and that the rate of neutralisation by hydroxyl ion leads to a catalytic constant for this ion in good agreement with the relationship between catalytic activity and basic strength that is found for other bases. Pedersen argues convincingly from this that the neutralisation of nitromethane actually proceeds as follows

$$CH_3NO_2 + OH^- \xrightarrow{slow} H_2O$$

$$+\bar{C}H_2.NO_2 \xrightarrow{inst.} CH_2 : NO_2^-$$

and that the slow process is the transfer of a proton from the nitromethane to the hydroxyl ion.

Assuming this mechanism, the reaction affords an excellent method of studying the problem that we have outlined. Thus if nitroethane (which has been shown by bromination experiments to contain two exchangeable hydrogen atoms) be neutralised in heavy water the following reactions will occur:

$$CH_3.CH_2NO_2 + OD^- \rightarrow CH_3CH : NO_2^- + HOD \quad (1a)$$

$$CH_3CH : NO_2^- + OD_3^+ \rightarrow CH_3CHDNO_2 \quad (1b)$$

$$CH_3.CHDNO_2 + OD^- \rightarrow CH_3CD : NO_2^- + HOD \quad (2a)$$

$$CH_3CD : NO_2^- + OD_3^+ \rightarrow CH_3CD_2NO_2 \quad (2b)$$

$$CH_3.CD_2NO_2 + OD^- \rightarrow CH_3CD : NO_2^- + D_2O. \quad (3)$$

In stage (1a) the deuteroxyl ion will remove a proton from the pseudo-acid while in stage (1b) a deuton will be transferred back: in stage (2a) the deuteroxyl ion will remove either a proton or a deuton, depending upon the relative rates of the two reactions. If the rate of proton transfer is much greater than that of deuton transfer then the former will occur quantitatively and since the number of removable protons is one-half that in the original compound the rate of neutralisation in stage (2a) will be one-half the rate in stage (1a). In the third stage, if the separation of protons has been virtually complete, there will be left only deuterium atoms that can ionise and the measured rate will be that of deuton transfer.

Experimental

In ordinary water the reaction can be followed by measurement of the electrical conductivity of the solution since the mobility of the hydroxyl ion is much greater than that of any other anion and consequently the conductivity falls off as the reaction proceeds. By analogy with the mobility of the deuteroxonium ion[4] it was expected that a similar condition of affairs would obtain in heavy water and this was found to be true.

The general method was to add to a solution of nitroethane in a conductivity cell a measured amount of baryta solution and to measure the electrical resistance at intervals of a minute or so. When the reaction was complete just sufficient sulphuric acid was added to precipitate all the barium and the reaction could then be followed again after addition of more baryta solution.

The experimental difficulties were mainly associated with the problem of working with small quantities of solution. The cell employed had a total capacity of about 5 cc but less than 0.5 cc completely covered the electrodes and further additions only slightly affected the cell constant which was found to be 2.085 in terms of Kohlrausch's data for KCl. Solutions of nitroethane were made up directly in the cell by weighing about 2–4 milligrams of nitroethane and adding water. Solutions of baryta were prepared by weighing barium oxide and water in a stoppered tube: analysis by titration with acid showed the barium oxide to be 78 percent BaO. Sulphuric acid solutions were prepared by

[3] Pedersen, Det Kgl. Danske Vid. Selskab. Math.-fys. Medd. **12**, 1 (1932).

[4] Lewis and Doody, J. Am. Chem. Soc. **55**, 3504 (1933).

weight from concentrated H_2SO_4 which by analysis was found to be 95.8 percent pure. Additions of baryta solution to the cell were made by means of a 1 cc syringe pipette which could be read to 0.002 cc and which was found to be accurate to the same limit. This was found to be a very convenient instrument, as from it the solution could be delivered practically instantaneously.* Additions of sulphuric acid were made by means of a microburette which held about 0.1 cc and could be read to 0.0003 cc. With this burette it was possible to carry out a conductivity titration of 0.5 cc of baryta solution (approx. N/10) with sulphuric acid (1 N) with an accuracy of about 1 percent. Several such titrations were made to check the experimental method.

Since the reaction is rather rapid the measurements were made at 0°C and it is interesting that although the freezing point of heavy water is 3.8°C the solutions never froze. Dr. Selwood informs me that this is in agreement with his experience that heavy water shows considerable supercooling.

In all the runs nearly equivalent amounts of nitroethane and alkali were employed but it was found that in most runs the values of k calculated from the expression

$$k=(1/at)\cdot(r_\infty/r_0)\cdot[(r-r_0)/(r_\infty-r)]$$

showed a marked increase with time. This was due to the reactants not being present in exactly equivalent amounts and as half of the reaction was usually over before the first reading was made the effect of slightly different concentrations was rather pronounced. Fortunately it was found that a linear relation obtained between the time and the apparent constant and that extrapolated values for zero time were in good agreement: this was specifically tested by varying the relative amounts of nitroethane and alkali.

Several runs were made in ordinary water in order to test the experimental procedure. One run in which a standard solution of NaOH was used gave a constant of 37.5 moles minutes^{-1}: the other runs with baryta gave values of which the mean was 39.0±5 percent. It was found that successive neutralisations of the same sample of nitroethane, as carried out in the heavy water experiments, gave values of k which were identical within the experimental error.

The conductivity of $Ba(OH)_2$ at 0°C was incidentally determined and found to vary from $\Lambda=95$ at $c=0.185$ N to $\Lambda=123$ at 0.031 N; the specific conductivity of the water was 1×10^{-6} ohm^{-1}.

The heavy water employed was distilled from alkaline permanganate and twice from BaO: its density was 1.1059 at 20° and its specific conductivity 3×10^{-6} ohm^{-1}. With this water 3 cc of 0.054 N $Ba(OD)_2$ solution (the strength was calculated by using the previous analysis of BaO) and 0.3 cc of 1.120 N D_2SO_4 were prepared. 0.42 cc of the $Ba(OD)_2$ solution was then placed in the conductivity cell and the conductivity determined at two concentrations, 0.0267 and 0.0201 N; the mean value of Λ was found to be 71.5. The solution in the cell was then titrated with the sulphuric acid solution by using the conductivities as the indicator of the end point: 0.0200 cc of acid was added leading to a value of 0.0534 N for the strength of the original $Ba(OD)_2$ solution.

One series of runs was made with nitroethane in heavy water and the results are summarised in Table I.

TABLE I.

Weight of nitroethane	0.00167 g
Weight of added D_2O	0.505 g
1. 0.42 cc $Ba(OD)_2$ added Added 0.0200 cc of D_2SO_4 to precipitate Ba.	$k=60$
2. 0.42 cc $Ba(OD)_2$ added Added 0.0200 cc of D_2SO_4	$k=36$
3. 0.42 cc $a(OD)_2$ added Added 0.0200 cc of D_2SO_4	$k=15.3\rightarrow9.2$
4. 0.42 cc $Ba(OD)_2$ added	$k=9.5\rightarrow6.0$

In stages 3 and 4 there are marked decreases in the values of k as the reaction proceeds. This can be explained if we suppose that the replacement of protons by deutons is not quite complete and that in consequence there are two types of molecule reacting at different rates and making the observed velocity constant greater at the beginning of the reaction than at the end. This also explains why the rate in stage 4 is less than in stage 3.

* For the loan of this pipette I am indebted to Professor W. W. Swingle of the Biology Department, Princeton.

From the results we can draw the following conclusions: (a) the reaction proceeds in separate stages as anticipated; (b) the rate of proton transfer is at least 10 times as great as that of deuton transfer when both are determined under the same conditions; (c) the rate of proton transfer to a deuteroxyl ion in heavy water is about 50 percent greater than the rate of transfer to a hydroxyl ion in ordinary water.

Although the results were obtained at 0°C it is probable that these conclusions will be equally applicable at room temperature and other temperatures not far remote and it is of interest to consider them in relation to certain other results recently recorded.

Moelwyn-Hughes and Bonhoeffer[5] have found that the catalytic effect of hydrogen ions on the inversion of sucrose in 90 percent D_2O is about 60 percent greater than in ordinary water. This increase in rate is analogous to conclusion (c) given above and in conjunction with conclusion (b) enables us to exclude definitely as the rate determining process the transfer of hydrogen ion (proton or deuton) from the catalyst to the sucrose molecule. The simplest explanation is that there is an equilibrium of the type

$$\text{Sucrose}+\text{Acid}\rightleftharpoons[\text{Sucrose H}]^+ + \text{Base}$$

and that the rate of inversion is determined by the rate of decomposition of the complex $[\text{Sucrose H}]^+$: the velocity constant would then be given by $k=(C_{\text{H}}{}^+/K)\cdot k'$ where $C_{\text{H}}{}^+$ is the hydrogen ion concentration, K is the dissociation constant of the sucrose ion, k' is the velocity constant for the decomposition of the sucrose ion. The relative catalytic constants for the hydrogen ion in heavy water and ordinary water will then be given by

$$\frac{k_{\text{D}_3\text{O}^+}}{k_{\text{H}_3\text{O}^+}}=\frac{K_{(\text{H}_2\text{O})}}{K_{(\text{D}_2\text{O})}}\cdot\frac{k'_{(\text{D}_2\text{O})}}{k'_{(\text{H}_2\text{O})}}.$$

The fact that $k_{\text{D}_3\text{O}^+}$ is greater than $k_{\text{H}_3\text{O}^+}$ may then be accounted for if $K_{(\text{D}_2\text{O})}$ is less than $K_{(\text{H}_2\text{O})}$.

If, however, the increase observed by Moelwyn-Hughes and Bonhoeffer and that recorded here have a common explanation, this must be sought in the variation of one or more of the terms in the equation

$$v=Ze^{-A/RT}c_A\cdot c_B\cdot f_A f_B/f_{(AB)},$$

where Z is the collision number, A the activation energy, c_A, c_B the concentrations of the reactants, and f_A, f_B, $f_{(AB)}$ the activity coefficients of the reactants and the critical complex.

If the increased rate is due to a change in the activity factor we should expect this to be not greater than the change in the solubility of a uni-univalent salt but actually the change is about four times as great[6] so it is probable that a change in the activation energy is the important factor. As pointed out by Topley and Eyring[7] it is possible for the difference in zero point energies between a proto- and deuto-compound to be greater in the activated than in the normal state and this may occur in solution due to differing degrees of hydration.

Whatever may be the explanation of the increased velocity observed in heavy water the fact that there is no decrease in the catalytic constant for the inversion of sucrose is in agreement with previous observations that there is no generalised acid catalysis but only a specific effect of the hydrogen ion on the inversion process. It is evident that a mechanism such as that suggested above makes the effect of any acid indistinguishable from that of a hydrogen ion.[8]

The other important result is that of Pacsu[9] who has shown that in 60 percent D_2O the rate of mutarotation of α-glucose is reduced to 0.53 of its value of H_2O while in pure D_2O the value is about one-third. Since the mutarotation is catalysed by acids and bases[10] and, as shown by Pedersen[11] the "spontaneous" reaction is really a basic catalysis by water molecules, it was of

[5] Moelwyn-Hughes and Bonhoeffer, Naturwiss. **22**, 174 (1934).

[6] Cf. Taylor, Caley and Eyring, J. Am. Chem. Soc. **55**, 4334 (1933).

[7] Topley and Eyring, J. Chem. Phys. to appear shortly.

[8] Hammett and Paul (J. Am. Chem. Soc. **56**, 830 (1934)) have tentatively suggested that at very high concentrations the molecule of trichloracetic acid has a catalytic effect but this is very doubtful.

[9] Pacsu, J. Am. Chem. Soc. **55**, 5056 (1933); **56**, 745 (1934).

[10] Cf. Brönsted and Guggenheim, J. Am. Chem. Soc. **49**, 2554 (1927); Lowry and Smith, J. Chem. Soc. **48**, 2539 (1927).

[11] Pedersen, Den almindelige Syre og Base-Katalyse, Copenhagen, 1932.

interest to determine the effect of D_2O on the acid catalysis. This was done under the direction of Professor Pacsu and the following results were obtained. (Table II.)

TABLE II. *Mutarotation of glucose.*

Temperature 23.3°C	Concentration of α-glucose 5%
Solution	k ($\log_{10}$ mins.$^{-1}$)
H_2O	0.0089
+0.102 N HCl	0.0328
D_2O (+10^{-4} N HCl)	0.00232
+0.0051 N HCl	0.00320
+0.0095 N HCl	0.00410

The HCl solutions were prepared by adding constant boiling acid.

The values derived for the catalytic constants of H_2O and OH_3^+ are 0.0089 and 0.24 in close agreement with the values interpolated from the data of Hudson and Dale.[12]

The results for heavy water lead to values of 0.0023 and 0.18, respectively, for the catalytic coefficients of D_2O and OD_3^+, and hence the catalytic activity of the H_2O molecule is 3.8 times as great as that of the D_2O molecule whereas the activity of OH_3^+ is only 1.33 times that of OD_3^+. This is explicable in terms of Pedersen's hypothesis that the effect of the H_2O molecule is that of a basic catalyst.

We are now in a position to discuss the mechanism of the mutarotation of glucose and we take as the starting point the experimentally established fact that the unimolecular constant for the mutarotation of α-glucose is identical with that for β-glucose and that the observed constant is therefore $k=k_\alpha+k_\beta$. Further Lowry has shown that mutarotation requires both an acid and a basic catalyst and Pedersen[11] has set up on this basis the following schemes for the basic and acid catalysis, respectively.

(1) $\mathrm{B}+\alpha-\mathrm{HG}\rightleftharpoons\mathrm{A}+\alpha-\mathrm{G}^-$ (a)

$\alpha-\mathrm{G}^-\rightleftharpoons\beta-\mathrm{G}^-$ (b)

$\beta-\mathrm{G}^-+\mathrm{A}'\rightleftharpoons\beta-\mathrm{HG}+\mathrm{B}'$ (c)

(2) $\mathrm{A}+\alpha-\mathrm{HG}\rightleftharpoons\mathrm{B}+\alpha-\mathrm{HGH}^+$ (a)

$\alpha-\mathrm{HGH}^+\rightleftharpoons\beta-\mathrm{HGH}^+$ (b)

$\beta-\mathrm{HGH}^+\rightleftharpoons\beta-\mathrm{HG}+\mathrm{A}'$ (c)

[11] Hudson and Dale, J. Am. Chem. Soc. **39**, 320 (1917).

Equilibrium (b) in each case is supposed to be set up very rapidly and the unimolecular changes that occur can therefore be written

$$\alpha-\mathrm{GH}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}1^-\xrightarrow{k_2}\beta-\mathrm{GH}$$

and k_α (or k_β) the overall constant for one form going over into the other is then given by

$$k_\alpha=k_1k_2/(k_{-1}+k_2)$$

and we may distinguish three possibilities: (1) $k_{-1}\ll k_2$ and $k_\alpha=k_1$. In this case the measured rate is simply that of proton (or deuton) transfer and should therefore be reduced in D_2O according to our results, to about one-sixth of the value in H_2O. However, at the beginning of the reaction this would not apply for the conversion of the α-glucose which could lose only protons, and consequently, as the reaction proceeds, the velocity constant should fall off. Such an effect is not observed nor is the reduction in rate as great as one-sixth and hence this possibility is excluded. (2) $k_{-1}\sim k_2$ and $k_\alpha=k_1/(1+k_{-1}/k_2)$. This condition would also involve a change in the constant during the progress of the reaction and so must be excluded. (3) $k_{-1}\gg k_2$ and $k_\alpha=(k_1/k_{-1})\cdot k_2$. Since k_1/k_{-1} involves the dissociation constant of either the glucose cation or of glucose itself while k_2 is the rate at which a proton (or deuton) is added to or removed from the intermediate complex this mechanism can be made to fit the facts.

It may also be suggested on the basis of this work that the exchange of deuterium and protium atoms in a homogeneous phase at ordinary temperatures is essentially an acid-base catalyzed reaction and probably the most expeditious method of promoting such an exchange is to add alternately acid and alkali.

I wish to express my gratitude to Professor Hugh S. Taylor, for the facilities offered me in this laboratory and to him as well as other members of the laboratory for helpful discussions.

I am also indebted to the Leverhulme Trustees for a fellowship and to the University of Reading, England, for leave of absence.

On Electrolytes in Media of Low Dielectric Constant

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A conductance function derived by Halpern and Gross is compared with experimental data for what they consider to be the most favorable case: slight dissociation in a solvent of very low dielectric constant, at concentrations near that of the minimum in conductance. Such comparison shows that the functional form required by their equation is not satisfied by the data for tetraisoamylammonium picrate in benzene over the concentration range $1\times10^{-6}-2\times10^{-4}N$. It is pointed out that the Bjerrum radius is not of decisive importance in the interpretation of conductance data.

IN a recent number of this journal, Halpern and Gross[1] present a theoretical treatment of electrolytic solutions, which is based on "ion-dipole" interaction, and in a succeeding paper in the same number of the journal, Gross and Halpern[2] undertake a "theoretical interpretation of the experimental results obtained by Fuoss and Kraus," this interpretation being made in the light of their theory. They criticize our own interpretation[3] of our experimental results in terms of "ion association" and conclude that "the formulae of Kraus and Fuoss can only be considered to be empirical laws," while they hold that their own theory reproduces "quantitatively several features of the conductivity phenomena." It will be unnecessary for us to offer any criticisms of the theoretical foundations of the Halpern-Gross theory since, as we shall show, it does not reproduce the experimental data. We must take exception, however, to their statement that our formulae are merely empirical laws, since they have obviously arrived at their conclusions through misinterpretation of the physical picture underlying our description.

To consider first the applicability of the Gross-Halpern theory to the experimental data, we consider their Eq. (9), which they use "to explain conductivity phenomena in media of low dielectric constant" and for which they claim "that the agreement is best for very low dielectric constants and near the minimum of dissociation." The equation is

$$\log \gamma^2 c = A + Bc. \qquad (1)$$

Our limiting conductance equation, for which we make the same claims, is

$$\Lambda\sqrt{c} = \alpha + \beta c. \qquad (2)$$

Gross and Halpern show a plot of Eq. (1) applied to our data for the conductance of tetraisoamylammonium nitrate in dioxane.[4] If the equation is applicable, the plot should be linear. At best, the plot is linear for a concentration ratio of 1 : 3 and if the plot is carefully constructed, it is evident that it exhibits curvature over the whole range. A much more conclusive test of the equation could have been obtained by applying it to the conductance of tetraisoamylammonium picrate in benzene,[5] for which we have published data to concentrations as low as $10^{-6}N$. In Fig. 1 are plotted Halpern and Gross' function (1) and our own function (2) for solutions of the picrate in benzene for the concentration interval 1×10^{-6} to 2×10^{-4}. Inspection of the figure will show that, while our Eq. (2) yields a linear plot over the entire concentration range, the Halpern and Gross Eq. (1) shows a marked curvature over the entire range. At best, their equation might be applicable in the case of very small concentrations, because it can readily be shown that (1) and (2) have the same form at concentrations well below that of the minimum. An extrapolation of their function from the concentration range where it approximates linearity is shown by the dotted line in the figure. The conclusion of Gross and Halpern that their formula "gives satisfactory results principally for the region close to the minimum-conductivity" is clearly untenable. On the plot, the position of the

[1] Halpern and Gross, J. Chem. Phys. **2**, 184 (1934).

[2] Gross and Halpern, J. Chem. Phys. **2**, 188 (1934).

[3] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 476, 1019, 2387 (1933).

[4] Kraus and Fuoss, J. Am. Chem. Soc. **55**, 21 (1933).

[5] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 3614 (1933).

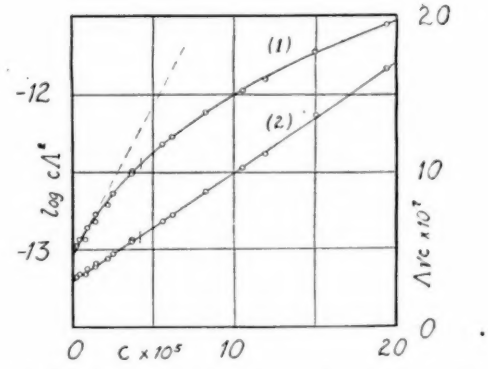

FIG. 1. Conductance of tetraisoamylammonium picrate in benzene at 25°; (1) Halpern and Gross function $\log c\gamma^2 = A + Bc$; (2) Fuoss and Kraus function $\Lambda\sqrt{c} = \alpha + \beta c$.

minimum is indicated by vertical lines crossing the curves.

In passing, we may point out that in attempting to fit their theory to our experimental data, they have found it necessary to assume for their "molecules" a value of the moment $\mu = 5.8 \times 10^{-18}$. This value is of the same order of magnitude as that of ordinary neutral polar molecules. The values found by Kraus and Hooper[6] for electrolytes are several times larger. This discrepancy seems serious, because the parameter μ appears as an exponent in the coefficient of c in their formula (8).

On the theoretical side, the criticisms of Gross and Halpern are largely concerned with the hypothesis of ion association and center around the Bjerrum radius R. Actually, the Bjerrum radius R is not fundamental to our theory, as one of us has already shown;[7] it is merely a convenience introduced for the purpose of approximate calculation and, if necessary, can be dispensed with altogether.[8] However, since the criticisms of Gross and Halpern are directed at our use of the Bjerrum radius, we may be permitted to develop this picture and to indicate how the criticisms of Gross and Halpern fail to apply. Detailed discussions will be found in papers already published or in papers which will appear shortly.

In solvents of high dielectric constant and at low concentrations, it is possible to account for many of the properties of electrolytic solutions by means of the time average potential of the ionic atmosphere as proposed by Debye and Hückel. As the dielectric constant of the solvent is decreased, the potential energy of a given pair of ions at contact increases, and when it becomes equal to and greater than kT, we may expect that ion pairs will have a finite chance of existing as stable structures. We assumed that such pairs are non-conductors (unless a third ion is present at short distances, which will produce a triple ion) and have shown that by means of this simple picture it is possible to account quantitatively for conductance data over a wide range of all variables.[9]

We then sought a plausible mechanism for the assumed reaction

$$A^+ + B' \rightleftharpoons AB$$

and found that the Coulomb force law was sufficient[10] to account for the observed energies of dissociation as calculated from experimental K values, provided some device were introduced to force convergence of the phase integral. Breaking the integral at the Bjerrum limit $R = \epsilon^2/2Dkt$ was chosen as the simplest method; this step is, however, a numerical approximation and is not an essential element in our theory. When two ions are far apart, other molecules and ions between screen the ions so that their effects on each other decrease integrably.[11]

In any case, when the dielectric constant of the solvent is small, the principal contribution to our calculated K values are due to the exponential peak near $r = a$ (contact) and the integral is numerically *independent* of the upper limit, so long as it is not of order infinity.

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[6] Kraus and Hooper, Proc. Nat. Acad. Sci. **19**, 939 (1933).

[7] Fuoss, Phys. Zeits. **35**, 59 (1934).

[8] We might point out that elimination of the Bjerrum radius will not "invalidate the application of the theory to media of low dielectric constants." Our variation of K with DT comes from the limit $r = a$ in our integration, as inspection of Eq. (7) of our third paper (J. Am. Chem. Soc. **55**, 1019 (1933)) will show.

[9] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 476 (1933).

[10] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 1019 (1933).

[11] Fuoss, Phys. Zeits. **35**, 59 (1934). Further work on this problem is in progress; and in a forthcoming publication (J. Am. Chem. Soc. **56**, 1027 (1934)), a method is given for the calculation of osmotic properties of an associated electrolyte, which is independent of the Bjerrum radius. The convergence problem is also discussed in some detail in the papers mentioned in this footnote.

Extending our physical picture along the same lines, we next assumed the triple ion equilibrium[12] as the interaction of next order of importance, and found that it quantitatively accounted for the minimum in conductance. We again used the analogue of the Bjerrum radius, but are able to show that the precise value of the upper[13] limit is unimportant.

Gross and Halpern, however, seem to read into our papers the statement that nearly all of the ion pairs consist of ions at a distance of $R=\epsilon^2/2Dkt$ from each other, thus: "The 'molecules' in Bjerrum's theory of ionic association have a 'radius' R which for media of low dielectric constant (e.g. dioxane $D=2.2$) takes a value 1.3×10^{-6} cm. Since almost all the salt dissolved is forming 'molecules' the volume accessible to the 'free ions' becomes very much reduced (sometimes even negative); the free energy of the ions therefore is very much increased as compared with the value it would take if the total volume were accessible to the ions." We point out the fact that the ratio p of the probability that two ions are at contact to the probability that they are at a distance R from each other is

$$p=(a^2/R^2)\exp(\epsilon^2/aDkT-\epsilon^2/RDkT)$$

In dioxane, with $a=6\times10^{-8}$ and $R=127\times10^{-8}$,

$$p=(36/16{,}100)e^{42.3-2}=2.24\times10^{-3}e^{40.3}=7\times10^{14}.$$

It therefore appears that ions at contact are enormously more probable configurations than "molecules" containing ions at $r=R$. In dilute solutions in solvents of low dielectric constant, ions will either be in contact, or if they are free, they will be at distances greater than R from other free ions, except for a very small number of transition cases. Suppose we *do* assign a volume $v=(4\pi R^3/3)$ to each ion, and assert that an ion pair will form if two such spheres intersect. For $R=1.27\times10^{-6}$ cm, $v=8.6\times10^{-18}$ cm^3. If we had Gross and Halpern's "actual case of practical interest: a (*thousandth*) normal[14] solution of tetraisoamylammonium nitrate in dioxane," and *if* the salt existed completely in the form of such "molecules," then the volume excluded would be $Nv=5000$ cc. As a matter of fact, we applied our limiting equations to dioxane solutions of concentrations of the order of $10^{-4}N$, where the degree of dissociation was about $3\times10^{-5}/100=3\times10^{-7}$ (if we use round values: $\Lambda=3\times10^{-5}$, $\Lambda_0=100$), so that the free ion concentration is about 3×10^{-11}. This corresponds to an excluded volume of $3\times10^{-11}\times Nv=2\times10^{-4}$ cc per liter of $10^{-4}N$ solution. To this, we add a volume of $10^{-4}N.2$. $(4\pi a^3/3)\approx0.11$ cc corresponding to the ion pairs assumed to be pairs at contact. Gross and Halpern would have us exclude a volume v for each ion pair, while the probability calculation made above indicates that ion pairs are predominantly ions in contact.

We wish also to correct several erroneous statements appearing in the paper by Gross and Halpern. They state "... they (Fuoss and Kraus) have to assume for example that a molecule and an ion are bound to a triple ion even though the binding energy in some cases is smaller than kT ...." We are unable to find any binding energies for triple ions that are less than kT. In Table III of our fourth paper, the smallest (numerical) value of log $_{10}k_3$ is 1.56 which corresponds to log nat $k_3=3.58$. This is equivalent to a dissociation energy of about $3kT$ per triple ion, that is, twice the average kinetic energy. In this case the dissociation of triple ions was so nearly complete that we were unwilling to assign an experimental value to the constant. Again, quoting: "the main points which Fuoss and Kraus consider as experimental verification of Bjerrum's ionic association may be enumerated as follows: (a) with a suitably chosen value a_1 for the minimum distance of approach between the ions it is possible to calculate the variation of the logarithm of the molecular dissociation constant for changes in the dielectric constant of the medium; the following relation is found to hold:

$$\log K_1\sim1/D."$$

[12] Fuoss and Kraus, J. Am. Chem. Soc. **55**, 2387 (1933).

[13] Since the details of this investigation will be published shortly, it seems unnecessary to reproduce them here.

[14] The editor informs us that the original statement of Gross and Halpern contains a misprint, and that it should read "a thousandth normal solution." We therefore have made the correction in the quotation. It is unfortunate that the misprint was not noticed in proof, because it gives the impression that we expect our formulas to apply to normal solutions. Our present equations cover concentrations only up to the neighborhood of the minimum in conductance, which for tetraisoamylammonium nitrate in dioxane appears at about $3\times10^{-5}N$.

And again: "The fact that the logarithm of the dissociation constant varies proportional to $1/D$, and that this variation is implied in Bjerrum's picture cannot be thought to corroborate the latter." Reference to Eq. (7) of our third paper will show that the logarithm is not proportional to $1/D$ but that

$$\log K \sim \log D + A/D.$$

This formula covers a range of experimental data to which the simple equation cited by Gross and Halpern does not apply.

In conclusion, we wish to point out that our formulation of the problem of electrolytic solutions provides a simple and consistent picture of these solutions which reproduces the experimental data over a wide range of conditions. In contrast, the theory of Halpern and Gross fails to reproduce experimental observations even in a narrow range of concentration, and in solvents of lowest dielectric constant.

Heat Capacity Curves of the Simpler Gases. VI. Rotational Heat Capacity Curves of Molecular Deuterium and of Deuterium Hydride. The Equilibrium Between the Ortho and Para Forms of Deuterium. Free Energy, Total Energy, Entropy, Heat Capacity and Dissociation of H^2H^2 and of H^1H^2, to 3000°K[1]

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Heat capacities, entropies, free energies, total energies and dissociation constants have been calculated for H^2H^2 and for H^1H^2, to 3000°K, by reliable methods and are listed in tabular form. The ortho-para equilibrium in H^2H^2 has been considered for both the gaseous and the solid states. The solid state equilibrium has been discussed from the point of view of its bearing on the application of the third law of thermodynamics. The rotational heat capacity curves of the various forms of H^2H^2 and that of H^1H^2 are shown graphically and are compared with the rotational heat capacity curve of ordinary hydrogen and with the hypothetical rotational specific heats of gaseous nitrogen. The heavy molecules, H^2H^2 and H^1H^2, dissociate to only about one-half the extent of H^1H^1 below 3000°K. The three hydrogen molecules are compared with respect to the influences of molecular stretching and of anharmonic vibration in the high temperature heat capacities. We also include tables which show the distributions of molecules among the vibrational levels as a function of the temperature.

THE growing importance of deuterium and its compounds, and its increasing availability, warrant the preparation of accurate and extensive tables of its thermodynamic properties. Particular interest also attaches to the rotational heat capacity curves of molecular deuterium, which possesses ortho and para modifications, and of deuterium hydride, which exists in only one form.

We have carried out accurate calculations of this character by the summation method[1] which Davis and Johnston[1] have shown is, for the special case of hydrogen, *more rapid* than are approximation methods.[2]

The discrete energies, E_i, were calculated by the equation

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* Charles A. Coffin Research Fellow, 1933–34.

[1] Previous papers in this series have been published in the Journal of the American Chemical Society. These include calculations on NO [Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933)], on O_2 [Johnston and Walker, ibid. **55**, 172, 187 (1933)], on neutral OH [Johnston and Dawson, ibid. **55**, 2744 (1933)], on CO and N_2 [Johnston and Davis, ibid. **56**, 271 (1934)] and on ordinary H_2 [Davis and Johnston, ibid. **56**, 1045 (1934)]. The equations appropriate to the exact summation method, and the labor saving use of "corrected approximations," in obtaining sums for the excited vibrational levels, used again in this paper, are discussed in the paper by Johnston and Chapman. As we do not wish to employ space to repeat details of that treatment, the reader is referred to these earlier papers.

[2] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932); Johnston and Davis, ibid. **55**, 271 (1934); Kassel, J. Chem. Phys. **1**, 576 (1933); Gordon and Barnes, ibid. **1**, 297 (1933).

$$E_i = \omega_e(v+\tfrac{1}{2}) - X_e\omega_e(v+\tfrac{1}{2})^2 + [B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \delta_e(v+\tfrac{1}{2})^3] \times J(J+1) + [D_e + \beta_e(v+\tfrac{1}{2})]J^2(J+1)^2 + F_eJ^3(J+1)^3. \quad (1)$$

The molecular constants which we employed are given in Table I, and were computed from those of ordinary hydrogen[3] by the use of the established relationships between the constants of isotopic molecules.[4] For this purpose we employed the mass numbers 1.00778[5] and 2.01363[6] for protium and deuterium, respectively.

TABLE I. *Molecular constants of the heavy hydrogens (in cm^{-1}).*

	H^2H^2	H^1H^2
ω_e	3125.4	3826.6
$X_e\omega_e$	65.72	98.52
B_e	30.465	45.668
α_e	1.0859	1.9931
γ_e	0.01713	0.03850
$-\delta_e$	0.00115	0.00317
$-D_e$	0.01165	0.02618
β_e	1.80×10^{-4}	4.95×10^{-4}
F_e	6.49×10^{-6}	2.19×10^{-5}

Account was also taken of the one unit[7] of nuclear spin which is associated with the deuterium atom and which necessitates additional weight factors of 3 and 6, respectively, in the odd and even rotational states of the H_2^2 molecule.[8] The results of these calculations are given in the accompanying tables and figures.

[3] Jeppeson, Phys. Rev. **44**, 165 (1933).

[4] Cf. Jevons, *Report on Band Spectra of Diatomic Molecules*, Cambridge University Press (1932), p. 212, for a convenient summary of these. These relationships, which have been verified to within the limits of experimental accuracy for many molecules in which the effect is much smaller than for hydrogen, have also been verified in the spectra of neutral OH (unpublished data of Johnston and Dawson) in which the isotopic shifts are greater than in hydrogen. However, we do not mean to imply that the constants listed in Table I are necessarily reliable to the full number of significant figures to which they are published since, indeed, the constants of ordinary hydrogen are not that reliable. But a reasonable estimate of the uncertainty which attaches to these constants by reason of the relationships used in deriving them indicates that the influence on the values of the various thermodynamic properties lies within the precision to which the latter are expressed.

[5] Aston, Proc. Roy. Soc. **A115**, 487 (1927).

[6] Bainbridge, Phys. Rev. **44**, 57 (1933).

[7] Lewis and Ashley, Phys. Rev. **43**, 837 (1933).

TABLE II. *Low temperature heat capacities (C_P) of the heavy hydrogens (in the ideal gaseous state), in calories/mole/degree.*

T, degrees absolute	Pure ortho H^2H^2	Pure para H^2H^2	Equil. mixture of H^2H^2	Non-equil. mixture of H^2H^2	H^1H^2
0	0.000	0.000	0.000	0.000	0.000
10	4.970	4.970	5.009	4.970	4.970
15	4.970	4.970	5.286	4.970	5.053
20	4.972	4.970	5.696	4.970	5.371
25	5.004	4.970	6.048	4.992	5.872
30	5.107	4.970	6.277	5.061	6.376
40	5.626	4.980	6.629	5.410	6.996
50	6.425	5.034	6.943	5.961	7.149
60	7.176	5.159	7.175	6.503	7.124
70	7.663	5.353	7.295	6.893	7.076
80	7.864	5.592	7.325	7.107	7.036
90	7.859	5.844	7.295	7.187	7.012
100	7.745	6.086	7.243	7.192	6.998
120	7.447	6.472	7.132	7.122	6.984
140	7.219	6.715	7.054	7.051	6.979
160	7.090	6.848	7.010	7.010	6.976
190	7.007	6.934	6.983	6.983	6.974
220	6.982	6.961	6.975	6.975	6.975
260	6.976	6.972	6.975	6.975	6.976
300	6.977	6.977	6.977	6.977	6.978

THE ROTATIONAL SPECIFIC HEAT CURVES OF H^2H^2 AND OF H^1H^2

In Table II we give values of the molar heat capacity, up to 300°K, for the four possible types of gaseous deuterium and for deuterium hydride. The results are shown graphically in Figs. 1 and 2. It is interesting to compare Fig. 1 with Fig. 4 of Johnston and Davis[1] which gives the corresponding curves for nitrogen in the ideal gaseous condition. Except for temperature, the curves for the two gases are seen to be nearly identical, which is a consequence of their iden-

TABLE III. *Equilibrium distribution of deuterium molecules in ortho and para rotation states.*

T, °K	% Ortho	T, °K	% Ortho	T, °K	% Ortho
0	100.000	50	79.193	140	66.809
10	99.972	60	74.793	160	66.716
15	99.506	70	71.779	190	66.677
20	97.973	80	69.816	220	66.669
25	95.292	90	68.579	260	66.667
30	92.065	100	67.816	300	66.667
40	85.124	120	67.074		

[8] For the H^1H^2 molecule, on the other hand, there is no distinction in the weightings, as between odd and even rotational states. This is a consequence of the wave mechanics and is demonstrated, experimentally, in the spectra of $O^{16}O^{18}$ and $O^{16}O^{17}$. Giauque and Johnston, J. Am. Chem. Soc. **51**, 1436, 3528 (1929).

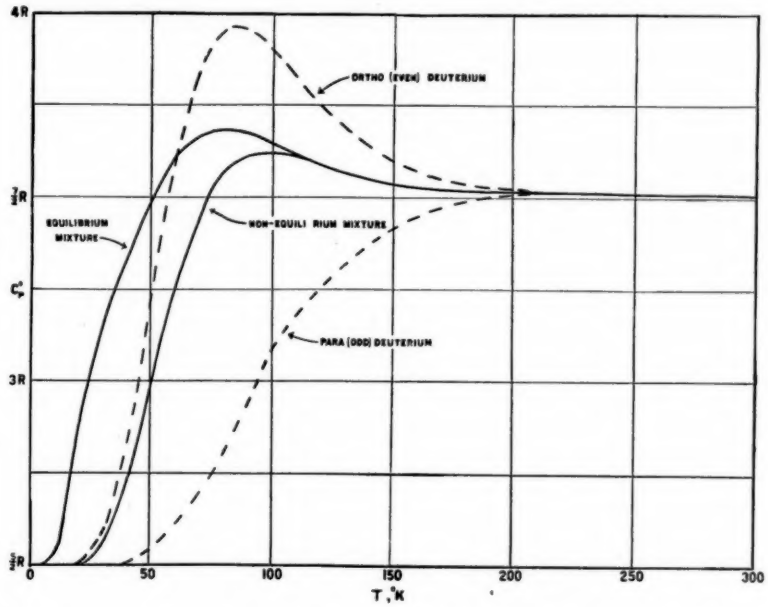

FIG. 1. Rotational portion of the heat capacity of deuterium, showing the influence of nuclear spin.

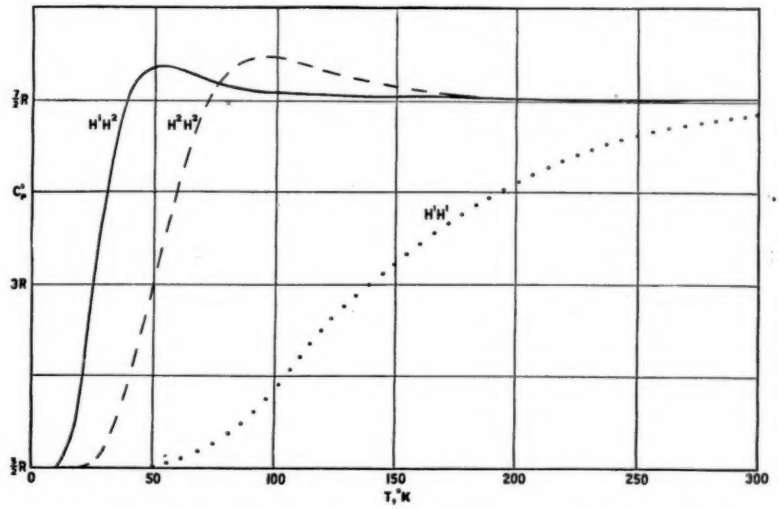

FIG. 2. Rotational portion of the heat capacity of H^1H^2 compared with the heat capacities of the normal (ortho-para) mixtures of H^2H^2 and of H^1H^1, respectively.

tical nuclear statistics. The rotational heat capacity curves for nitrogen are, of course, hypothetical since nitrogen condenses at a temperature much above that at which its various forms attain rotational equipartition. This makes the case of deuterium the more interesting since at least three of the curves in Fig. 1 may be realized experimentally. It is also interesting to compare our Fig. 1 with the corresponding figure for ordinary hydrogen[9] which possesses a different nuclear statistics.

Fig. 2 shows the rotational specific heat curve for H^1H^2 (for which only one curve exists) together with the ordinary ($\frac{3}{4}$ ortho, $\frac{1}{4}$ para for

[9] Cf. the diagram on page 193 of *Outlines of Atomic Physics*, Physics Staff of the University of Pittsburgh, John Wiley and Sons, New York, 1933, or plot the data of Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

H^1H^1; $\frac{2}{3}$ ortho, $\frac{1}{3}$ para for H^2H^2) non-equilibrium curves for the homonuclear gases. These latter are the curves which are measured under ordinary experimental conditions, with the gases prepared at room temperature.

The equilibrium distribution of deuterium molecules between ortho and para rotation states is given in Table III.

Free Energies, Total Energies, Entropies and High Temperature Heat Capacities

"Free energies," "total energies," entropies and high temperature heat capacities are given in Tables IV, V and VI. These calculations all refer to the ideal gaseous state at a pressure of one atmosphere and, for convenience in use at low temperatures, the tables of free energy and of entropy are given with nuclear spin contributions *included*.[11] In line with our usual custom, and that of Giauque and co-workers, we have employed the natural constants given in the *International Critical Tables*.[12, 13]

Table IV. *Values of* $-((F^\circ-E_0^\circ)/T)$ *for* H^2H^2, *for* H^1H^2 *and for atomic* H^2 *in the ideal gaseous state at 1 atmosphere (nuclear spin contributions included).*[10]

T, °K	H^2H^2	H^1H^2	H^2 (atomic)
20	15.366	14.479	—
25	16.529	15.613	—
50	20.397	19.439	—
100	24.739	23.788	—
150	27.447	26.602	—
200	29.400	28.391	—
250	30.926	29.901	24.428
298.1	32.133	31.099	25.302
300	32.176	31.137	25.334
400	34.157	33.110	26.763
500	35.698	34.645	27.871
600	36.961	35.902	28.777
700	38.033	36.968	29.543
800	38.965	37.895	30.206
900	39.792	38.715	30.791
1000	40.536	39.451	31.314
1250	42.131	41.025	32.423
1500	43.459	42.329	33.328
2000	45.610	44.435	34.758
2500	47.335	46.119	35.866
3000	48.782	47.533	36.771

Table V. $(E^\circ-E_0^\circ)$ *for gaseous* H^2H^2 *and for gaseous* H^1H^2 *(translational energy not included), in calories per mole.*

	H^2H^2				
T, °K	Pure ortho	Pure para	Equilibrium mixture	$\frac{2}{3}$ ortho $\frac{1}{3}$ para	H^1H^2
0	0.00	170.22	0.00	56.74	0.00
20	0.01	170.22	3.46	56.74	1.27
25	0.09	170.22	8.10	56.80	4.50
50	14.62	170.61	46.74	66.62	49.31
100	143.54	197.20	160.81	161.43	154.15
150	265.38	274.32	268.35	268.36	232.99
200	369.41	370.54	369.79	369.79	355.39
250	470.16	470.30	470.21	470.21	455.77
300	570.61	570.62	570.62	570.62	556.27
400	771.86	771.86	771.86	771.86	757.70
	H^2H^2	H^1H^2	T, °K	H^2H^2	H^1H^2
500	975.5	960.0	1250	2810	2666
600	1183.5	1164.3	1500	3581	3362
700	1399.3	1372.2	1750	4413	4129
800	1625.8	1585.5	2000	5299	4950
900	1865.1	1807.8	2500	7187	6734
1000	2118.1	2039.3	3000	9196	8658

Table VI. *Entropies (nuclear spin included) and molar heat capacities of* H^2H^2 *and of* H^1H^2 *in the ideal gaseous state (in calories/mole/degree).*

	H^2H^2		H^1H^2	
T, °K	S°	C°_p	S°	C°_p
298.1	38.731	6.977	37.954	6.978
400	41.054	6.985	39.972	6.985
500	42.616	7.019	41.532	6.998
600	43.901	7.081	42.810	7.025
700	44.999	—	43.896	7.072
800	45.965	7.294	44.844	7.143
1000	47.621	7.567	46.458	7.335
1250	49.346	—	48.124	7.619
1500	50.813	8.183	49.537	7.901
2000	53.227	8.600	51.877	8.357
2500	55.177	8.879	53.780	8.687
3000	56.814	9.083	55.386	8.936

[10] We have also computed many values of free energy which are omitted from the table in order to conserve space. The following empirical equations reproduce the free energy to within 0.001 or 0.002 calorie/mole/degree: *between 1000° and 3000°:*

For H^2H^2,

$$(F^\circ-E_0^\circ)/T=7.543-1.5R\ln T - R\ln(1-\exp(-1862.6/T))-1.4000\times10^{-5}T+8.1112\times10^{-9}T^2-9.6668\times10^{-12}T^3+1.5556\times10^{-15}T^4. \quad (2)$$

For H^1H^2,

$$(F^\circ-E_0^\circ)/T=8.598-1.5R\ln T - R\ln(1-\exp(-2257.7/T))+9.1667\times10^{-6}T-8.5000\times10^{-9}T^2-6.6667\times10^{-13}T^3. \quad (3)$$

These equations do not reproduce the correct values below 1000°.

[11] To obtain entropies or free energies with nuclear spin *excluded* the entropy or free energy values should each be decreased (numerically) by $R\ln 9$ (=4.366) for H^2H^2, $R\ln 6$ (=3.560) for H^1H^2 and $R\ln 3$(=2.183) for atomic deuterium. Calculations of equilibrium with nuclear spin entropy or free energy arbitrarily excluded are not permissible in reactions involving molecular deuterium, below 150°K.

[12] Int. Crit. Tab. Vol. I, p. 16.

[13] As a near approximation the values of thermodynamic properties computed with one set of natural constants may be converted to another set by multiplying through by the direct ratio of the values adopted for the gas constant R. This is a consequence of the fact that R enters as a factor in *all* of the entries in Tables II, IV, V and VI. The value of R

The values recorded in our Table VI are correct for either the equilibrium or the non-equilibrium mixtures of ortho and para deuterium. Those recorded in Table IV refer to the *equilibrium mixture* but above 100°K identical results are obtained for the non-equilibrium mixture.

We take the zero-point energy ($E_0°$) of each gas as that corresponding to the lowest available quantum state (here $v=0$, $J=0$) of H^2H^2 and of H^1H^2.

Urey and Rittenberg[14] have published short tables of the free energies of deuterium and of some of its compounds. When account is taken of the different set of natural constants[13] which were employed, and also of the slightly different molecular constants, close agreement is obtained for those temperatures for which the calculations are duplicated.

It is interesting to compare the contributions of molecular stretching and of anharmonic vibration to the high temperature heat capacities, for the three hydrogens. The comparison is given in Table VII. The figures for H^1H^1 are

TABLE VII. *Contributions of molecular stretching and of anharmonic vibration to the molar heat capacities of the hydrogens (calories/mole/degree).*

T, °K	Stretching H^1H^1	Stretching H^1H^2	Stretching H^2H^2	Departure from Hooke's law H^1H^1	Departure from Hooke's law H^1H^2	Departure from Hooke's law H^2H^2
1000	0.072	0.072	0.072	0.010	0.009	0.025
2000	0.135	0.136	0.135	0.097	0.101	0.138
3000	0.174	0.178	0.175	0.223	0.248	0.273

TABLE VIII. *Distribution of H^2H^2 molecules among the vibrational levels as a function of the temperature (°K).*

v	400°	600°	800°	1000°
0	99.998	99.92	99.51	98.57
1	0.002	0.08	0.48	1.40
2	0.000	0.00	0.01	0.02
3	0.000	0.00	0.00	0.00
v		1500°	2000°	3000°
0		93.98	87.66	74.53
1		5.59	10.66	18.54
2		0.38	1.43	4.92
3		0.05	0.21	1.39
4		0.00	0.03	0.42
Higher		0.00	0.01	0.10

given in the International Critical Tables, and used in these calculations, is 1.9869.

[14] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

TABLE IX. *Distribution of H^1H^2 molecules among the vibrational levels as a function of the temperature (°K).*

v	600°	800°	1000°
0	99.982	99.85	99.43
1	0.018	0.15	0.56
2	0.000	0.00	0.01
3	0.000	0.00	0.00
v	1500°	2000°	3000°
0	96.78	92.28	81.31
1	3.09	7.01	14.69
2	0.12	0.65	3.08
3	0.01	0.06	0.70
4	0.00	0.00	0.16
Higher	0.00	0.00	0.06

taken from Davis and Johnston.[1] Those for H^2H^2 and for H^1H^2 were calculated in the manner described in the same paper.

Tables VIII and IX show the distributions of molecules among the vibrational levels as a function of the temperature.

THE DISSOCIATION OF THE HYDROGENS

We have calculated dissociation constants, and percentage dissociations at a total pressure of 1 atmosphere, for H^2H^2 and for H^1H^2 by the relationships:

$$-R\ln K+\Delta F°/T=\left(\frac{F°-E_0°}{T}\right)_{atoms}-\left(\frac{F°-E_0°}{T}\right)_{molecule}+\frac{\Delta E_0°}{T} \quad (4)$$

and

$$100\alpha=100[K/(K+4P)]^{\frac{1}{2}}, \quad (5)$$

where 100α is the percentage dissociation. The values of $(F°-E_0°)/T$ are taken from our Table IV and from Table VII of Giauque.[9] $\Delta E_0°$ was taken to be 104,593±1000 cal. for the dissociation of H^2H^2, and 103,618±1000 cal. for the dissociation of H^1H^2.[15]

[15] These values are greater than that for H^1H^1 (102,800 ±1000) by the difference in the zero-point energies of vibration (1793 calories/mole and 818 cal./mole for H^2H^2 and H^1H^2, respectively, relative to H^1H^1) and rest on the assumption that there is a negligible isotope effect on the electronic terms of hydrogen. We are informed by Professor R. T. Birge (personal communication) that Dr. C. R. Jeppesen has found an electronic isotope effect of approximately 135 wave numbers in the A–C band system of H^1H^2. If, as Professor Birge suggests, this can be accounted

TABLE X. *Dissociation constants and percentage dissociations of hydrogen.*

T, °K	K H^1H^1	K H^1H^2	K H^2H^2
1000	64.49×10^{-19}	12.39×10^{-19}	9.27×10^{-19}
1500	36.00×10^{-11}	7.831×10^{-11}	6.747×10^{-11}
2000	29.60×10^{-7}	6.811×10^{-7}	6.227×10^{-7}
2500	6.915×10^{-4}	1.638×10^{-4}	1.542×10^{-4}
3000	26.87×10^{-3}	6.474×10^{-3}	6.187×10^{-3}

T, °K	Percent Dissociation (1 atmosphere) H^1H^1	H^1H^2	H^2H^2
1000	13×10^{-8}	5.6×10^{-8}	4.8×10^{-8}
1500	9.5×10^{-4}	4.4×10^{-4}	4.1×10^{-4}
2000	8.6×10^{-2}	4.1×10^{-2}	3.9×10^{-2}
2500	1.31	0.64	0.62
3000	8.1	4.0	3.9

The results of our calculations at five temperatures are given in Table X, in which we also include figures for the dissociation of H^1H^1, published by Giauque.[9]

It is interesting to note the nearly equal dissociation constants for the two heavier molecules and the fact that *both* of these molecules are considerably less dissociated than is the usual hydrogen. These relationships are not those that one would expect from classical considerations. Indeed, it is possible to show by the present method of treatment that at sufficiently high temperatures (temperatures at which $\Delta E_0^\circ/T$ becomes negligible) the two homonuclear molecules will have equal dissociation constants while K for H^1H^2 will be one-half of the K for either of the others. The relationships exhibited in Table IX are a consequence, primarily, of the difference in the zero-point energies of vibration and the nearly equal constants for the two heavier molecules over this range of temperature are a fortuitous consequence of the magnitude of the isotopic vibrational effects. If account is taken of the electronic isotope shifts referred to by Birge[15] the small differences that exist in the K's for H^1H^2 and for H^2H^2 will be somewhat increased.

for in terms of the electronic interaction discussed by Hughes and Eckert [Phys. Rev. **36**, 694 (1930)] and if account is also taken of the isotope effect on the zero-point energy of the *atom* (the zero-point energy of the H^2 atom is 84.4 cal./g atom less than for H^1), ΔE_0° for H^1H^2 will be some 50 calories larger than the value which we are using. A corresponding effect would be applicable to ΔE_0° for H^2H^2. The influence of these changes would be to further *decrease* the dissociation both of H^1H^2 and of H^2H^2, the decrease being the greater for the heavier molecule.

Urey and Rittenberg[14] have considered the reaction $H^1H^1+H^2H^2=2H^1H^2$, which is especially interesting at low temperatures. They found that, even at 700°K, the equilibrium constant for this reaction failed to attain the classical value of 4 by some 5 percent. We have calculated the constant at higher temperatures by the relationship

$$K=K_{11}K_{22}/(K_{12})^2, \qquad (6)$$

in which the K's with sub-numerals refer to H^1H^1, H^2H^2 and H^1H^2, respectively, and were taken from Table X. The results indicate that the constant for this reaction lies under 4 by about 3 percent at 1000°, 1 percent at 1500° and by about 0.5 of 1 percent at 3000°.

THE ENTROPY OF SOLID DEUTERIUM

Measurements of the heat capacities of solid and of liquid deuterium, together with the heats of fusion and of vaporization, are of interest in connection with the proper usage of the third law of thermodynamics. Four examples[16] are now known for which the correct values of entropy for use in thermodynamic calculations are not given by the $\int C_P dT$'s in conjunction with the ordinary application of the third law. One of these is ordinary hydrogen for which a correction amounting to $(R \ln 4+\frac{3}{4}R \ln 3)$ must be applied to the calorimetric value to obtain the absolute entropy. Of this amount, $R \ln 4$ is contributed by nuclear spin and at temperatures comparable to room temperature and above may be disregarded in the conventional usage of the third law, provided nuclear spin effects are excluded consistently for the other reactants and products as well. The remaining term, $\frac{3}{4}R \ln 3$, is a consequence of the rotational non-degeneracy of ortho hydrogen which goes into the solid state with one unit of rotational angular momentum which it holds down to about 2°K.[17]

There are four possibilities regarding the behavior of solid deuterium as a consequence of

[16] (a) H_2, Giauque and Johnston, J. Am. Chem. Soc. **50**, 3221 (1928); Phys. Rev. **36**, 1592 (1930); (b) NO, Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929); (c) CO, Clusius and Teske, Zeits. f. physik. Chemie **B6**, 135 (1929); Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932); (d), N_2O, Clusius, Nature **130**, 775 (1932).

[17] Simon, Mendelssohn and Ruhemann, Naturwiss. **18**, 34 (1930).

its nuclear statistics. (1) H^2H^2 may completely lose its nuclear spin entropy, amounting to $R \ln 9$ entropy units, in the process of freezing. This corresponds, physically, to the formation of a molecular crystal lattice in which the component molecules are composed of atoms whose respective spin momentum vectors are antiparallel to one another. In this event the values of entropy based on calorimetric measurements should be identical with those recorded in our Table VI, which include nuclear spin. (2) Para molecules may undergo transformation, at low temperatures, into the stable ortho form with its nuclear spin weighting of six. The entropy values obtained calorimetrically should then be lower than those given in Table VI by an amount $R \ln 6$. (3) The para molecules may lose the one unit of rotation which they possess in their ground state without, however, losing their identity. This would correspond to a molecular crystal lattice in which the para molecules (constituting $\frac{1}{3}$ of the total) would perform weak angular oscillations about fixed positions without making complete rotations.[18] In this event the calorimetric determinations of entropy should be lower than those given in Table VI by $R \ln 9$. This corresponds to the case actually observed for nitrogen[19] which possesses the same nuclear statistics as does deuterium. The formation of an atomic crystal lattice would lead to the same results. (4) The para molecules may retain their one unit of rotation in the crystal lattice while both para and ortho molecules retain their full spin multiplicity. This situation would lead to calorimetric values of entropy lower than those in Table VI by an amount $(R \ln 9 + \frac{1}{3} R \ln 3)$. This is analogous to the case of H^1H^1 although the numerical corrections are different.

Of these four possibilities, (1) and (2) are improbable and (4) is more probable than (3). Experimental heat capacity measurements would clearly distinguish between the several possibilities. It is also probable, assuming case (4) to be the actual situation, that H^2H^2 in the solid state would begin to lose the entropy associated with the rotation of its para molecules at a temperature somewhat above that at which the effect occurs for H^1H^1. This would bring the investigation of the effect into a more suitable experimental region than the one necessary for the investigation of ordinary hydrogen.

The calorimetric entropy of solid H^1H^2, in the pure state, is also of interest since it does not possess the possibilities of ortho-para influences which are responsible for the observed behavior of ordinary hydrogen and for the anticipated behavior of pure deuterium. We would expect the calorimetrically determined entropy of H^1H^2 to lie $R \ln 6$ entropy units below the values recorded in Table VI. We would not expect thermal effects similar to those observed at 2°K by Simon and co-workers to appear in solid H^1H^2 at temperatures above some very small fraction of a degree absolute.

We wish to acknowledge a grant-in-aid from the funds of the National Research Council which provided the electric calculating machine used in the preparation of this and other papers in this series.

Note added in proof.—An experimental paper by Jeppeson[20] on the spectrum of H^1H^2, which has appeared since the manuscript was submitted, gives molecular constants for H^1H^2 which are in excellent agreement with our Table I except for the value of β_e. Although we do not understand the discrepancy, since this constant depends on others in the list, the influence of the disagreement is negligible for even the precision to which the tables in this paper are given. An experimental paper by Farkas and Farkas[21] has also appeared with measurements of the ortho-para distributions at equilibrium in almost exact agreement with our Table III.

[18] Cf. Pauling, Phys. Rev. **36**, 430 (1930).

[19] Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).

[20] Jeppeson, Phys. Rev. **45**, 480 (1934).

[21] Farkas and Farkas, Science **79**, 204 (1934); Proc. Roy. Soc. **A144**, 481 (1934).

The Theory of Moderate Deviations from van't Hoff's Law

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(March 19, 1934)

A sketch of the application of van der Waals notions to the study of deviations from van't Hoff's law made by A. A. Noyes is given and a modification of the theory is introduced. An osmotic pressure equation is then deduced from a heat of formation equation. The new theory is shown to be, at least formally, in harmony with the old. Both theories result in an equation of the van der Waals type for osmotic pressures. This constitutes an extension of van't Hoff's very useful analogy between dilute solutes and gases.

THE phrase "dilute solutions" has come to refer particularly to solutions for which van't Hoff's theory is valid. Hence throughout this paper we shall use the term "near-dilute" to refer to solutions which although dilute are sufficiently concentrated to show deviations from van't Hoff's law.

I.

The equation

$$\pi(V-\beta)=RT, \tag{1}$$

in which π is the osmotic pressure, V the volume of a solution containing one mol of solute and β is a function of temperature, has been, probably, the most successful, empirically, of all the modified forms of van't Hoff's law. The observation of Morse and Frazer,[1] that better results are obtained in more concentrated solutions with van't Hoff's law if V is replaced by the volume of the solvent used to make up the solution, indicates only one way of using an equation of this type. In this case β is simply taken to be the difference between the volume of the solution and that of the solvent used to make up the solution.

The success of van der Waals in the field of gases under high pressure and of the van't Hoff analogy between dilute solutes and ideal gases made it inevitable that an attempt would be made to treat near-dilute solutions in the van der Waals fashion. This was done independently by Bredig[2] and Noyes.[3] We will give a sketch (in modern notation) of the theory of Noyes. Noyes was not interested in the variations of osmotic pressure with temperature and called anything that depended upon temperature only a constant. We will introduce temperature explicitly in our sketch.

In van der Waals gas equation we introduce as a correction to p, a term a/V^2 and as a correction to V a constant term b. Now in near-dilute solutions, Noyes assumed, we can neglect the attraction of solute molecules for each other and consider only the attraction between solute molecules and solvent molecules. The correction term to π will then be proportional not to the square of the concentration of the solute but to the product of the concentration of the solute and solvent. But since the concentration of the solvent is nearly constant we can simply take a/V for our correction term. In the correction term to V we shall have to consider both solute and solvent molecules. If we deal with an amount of solution containing one mol of solute and n_1 mols of solvent this term will be $b_2+n_1b_1$ in which the b's have a significance analogous to the b in van der Waals equation. Since

$$V=n_1\bar{v}_1+\bar{v}_2, \qquad n_1=(V-\bar{v}_2)/\bar{v}_1,$$

we have for the osmotic pressure of a near-dilute solution

$$[\pi-a/V][V-\{b_2+(V-\bar{v}_2)b_1/\bar{v}_1\}]=K, \tag{2}$$

in which K depends upon T alone. We can write this as

$$[\pi-a/V][V(1-b_1/\bar{v}_1)-(b_2-\bar{v}_2b_1/\bar{v}_1)]=K,$$

$$[\pi-a/V][V-\phi]=K', \tag{3}$$

[1] Morse and Frazer, Am. Chem. J. **34**, 28 (1905).
[2] Bredig, Zeits. f. physik. Chemie **4**, 444 (1889).
[3] A. A. Noyes, Zeits. f. physik. Chemie **5**, 53 (1890).

in which K' is a new function of temperature and

$$\phi=(b_2-\bar{v}_2b_1/\bar{v}_1)/(1-b_1/\bar{v}_1) \tag{4}$$

is approximately a constant. Noyes simplified Eq. (3) by multiplying out the left-hand side and noting that in the small term $a\phi/V$ we can take $1/V$ proportional to π and he introduced a proportionality "constant" but the proportionality factor is really $1/RT$. Introducing this we get

$$\pi[V-\phi(1-a/RT)]=K'+a, \tag{5}$$

$$\pi[V-\beta]=RT, \tag{6}$$

which is Eq. (1) with

$$\beta=\phi(1-a/RT). \tag{7}$$

We have put the right-hand side equal to RT for the equation must reduce to van't Hoff's in the limit as V increases at constant temperature.

Sackur[4] regarded Eq. (1) as closely analogous to Hirn's gas equation with β dependent only upon the "volume" of the solute and solvent molecules. He explained the absence of any term corresponding to van der Waals a/V^2 somewhat as follows: Since the osmotic pressure is independent of the nature of the semipermeable membrane, we can consider this to be infinitely thin. A solute molecule, then, at the instant it strikes the membrane is attracted by the solvent on one side of the membrane just about as much as by that on the other side. Both Noyes and Sackur gave extensive experimental tests of Eq. (1) using osmotic pressures determined both directly and indirectly. The results were excellent.

Now let us take Sackur's observation that the solvent on both sides of the membrane must be considered and consider anew the correction term to π. It is evident that in determining the effect of the attraction of solvent molecules for solute molecules we need to consider only the *excess* of solvent molecules in a given volume of pure solvent over those in the same volume of solution. If we start with a volume V of solution and remove the one mol of solute the decrease in the volume will be (approximately) $\bar{v}_2$. We can restore the volume to its initial value by adding Δn_1 mols of solvent where

$$\Delta n_1\bar{v}_1=\bar{v}_2$$

(approximately). The concentration of the "excess" molecules on the side of the pure solvent is then

$$\Delta n_1/V=(\bar{v}_2/\bar{v}_1)/V$$

and the correction factor to π will be (to a sufficient degree of accuracy)

$$-a'/V^2, \qquad a'>0,$$

in which we have absorbed $(\bar{v}_2/\bar{v}_1)$ into the proportionality constant. The sign will, of course, be the opposite to that of the correction term representing the attraction of the solute molecules for each other, which we shall introduce as (a/V^2). We have then in place of (3)

$$[\pi+a/V^2-a'/V^2][V-\phi]$$
$$=[\pi+\alpha/V^2][V-\phi]=RT \tag{8}$$

with

$$\alpha=a-a'. \tag{9}$$

(We again determine the right-hand side of the equation by considering its limiting form as V increases at constant T.) Multiplying out the left-hand side, neglecting the product of the two correction terms, $(\alpha/V^2)\phi$, and using the approximation $1/V=\pi/RT$ in the small term, $(\alpha/V^2)V$, we get

$$\begin{aligned}\pi[V-\phi+\alpha/RT]&=RT,\\ \pi[V-\beta]&=RT\end{aligned} \tag{10}$$

and we are again led to Eq. (1) with

$$\beta=\phi-\alpha/RT. \tag{11}$$

We shall show in the next section that this theory agrees with modern developments. These early papers present us with a very workmanlike approach to the problem of near-dilute solutions. They have been too long disregarded.[5]

[4] Sackur, Zeits. f. physik. Chemie **70**, 477 (1910).

[5] Van Laar, Kohnstamm, van der Waals and others have worked out a theory of binary solutions based upon van der Waals equation in great detail. (An excellent survey of this work is given in Vol. II of van der Waals-Kohnstamm's *Thermostatik*.) But they have considered van der Waals equation as one applicable to both gases and liquids and have applied it to the solution as a whole. Noyes and Bredig used van der Waals notions in the study of solutes considered as analogous to gases.

II.

Today we can approach the theory of near-dilute solutions from an entirely different standpoint. We can base the theory of any solution upon the equation[6]

$$\ln f_1 = \ln N_1 f_1^0 - \int_{(p,\ N_1)} [(\overline{H}_1 - H_1^0)/RT^2]dT \quad (12)$$

if we can determine $\overline{H}_1 - H_1^0$ as a function of T and N_2 (or N_1). (Throughout this paper we assume that the pressure upon the solution does not vary sufficiently to alter its properties.) If we take component one as the solvent and component two as the solute we shall have in a dilute solution

$$\ln f_1 = \ln N_1 f_1^0$$

and so in a near-dilute solution the correction term in (12) will be small and a rough approximation to the function $\overline{H}_1 - H_1^0$ will be sufficient. A number of different investigations[7] into the heat of formation, ΔH, of binary solutions, both theoretical and empirical, all agree in giving

$$\Delta H = A(T) N_1 N_2 \quad (13)$$

as the limiting form of the function for small values of N_2. (We can use Biron's relation,[8] $\Delta V = k N_1 N_2$, in which k is a constant, in connection with the equations of van Laar and Lorenz.) We shall consider the function $A(T)$ later.

Using the equation (No. (3) reference 6)

$$\overline{H}_1 - H_1^0 = (1 - N_1)[\partial \Delta H / \partial N_1]_{T,\ p} + \Delta H$$

we can obtain from (13) the equations

$$\left.\begin{aligned} \overline{H}_1 - H_1^0 &= A(T) N_2^2 \\ \overline{H}_2 - H_2^0 &= A(T) N_1^2 \end{aligned}\right\}. \quad (14)$$

In order to compare our results with the earlier theory as outlined and supplemented above, we shall deduce the dependence of the osmotic pressure of the solute upon the composition of the solution expressed in terms of V. The osmotic pressure will be given (with a sufficient degree of accuracy) by the equation[9]

$$\pi \bar{v}_1 = -RT \ln (f_1/f_1^0)$$

and using (12) and the first of Eqs. (14) we get

$$\begin{aligned} \pi \bar{v}_1 &= -RT \ln N_1 + N_2^2 T \int (A/T^2)dT \\ &= -RT \ln N_1 + B N_2^2 \end{aligned} \quad (15)$$

with

$$B = T \int (A/T^2)dT. \quad (16)$$

$$\begin{aligned} \text{Or } \pi \bar{v}_1 &= -RT \ln (1 - N_2) + B N_2^2 \\ &= RT(N_2 + \tfrac{1}{2} N_2^2 + \cdots) + B N_2^2 \\ &= N_2 RT + (RT/2 + B) N_2^2 \end{aligned}$$

approximately, since N_2 is small. Now

$$V = \frac{N_1 \bar{v}_1 + N_2 \bar{v}_2}{N_2} = \frac{\bar{v}_1 + (\bar{v}_2 - \bar{v}_1) N_2}{N_2} = \frac{\bar{v}_1}{N_2} + \bar{v}_2 - \bar{v}_1$$

$$N_2 = \frac{\bar{v}_1}{V + \bar{v}_1 - \bar{v}_2} = \frac{\bar{v}_1}{V} \frac{1}{1 + (\bar{v}_1 - \bar{v}_2)/V}$$

$$= \frac{\bar{v}_1}{V}(1 - (\bar{v}_1 - \bar{v}_2)/V) \quad (17)$$

approximately, since as long as N_2 is small, V will be very large compared to $\bar{v}_1 - \bar{v}_2$. This gives, neglecting powers of $1/V$ higher than the second,

$$\begin{aligned} \pi \bar{v}_1 &= \frac{RT \bar{v}_1}{V}(1 - (\bar{v}_1 - \bar{v}_2)/V) + (RT/2 + B)(\bar{v}_1/V)^2, \\ \pi &= \frac{RT}{V}[1 - (\bar{v}_1 - \bar{v}_2)/V + (\tfrac{1}{2} RT + B)\bar{v}_1/RTV] \\ &= \frac{RT}{V}[1 + \beta/V], \end{aligned}$$

where

$$\beta = B \bar{v}_1/RT + \bar{v}_2 - \bar{v}_1/2. \quad (18)$$

The term β/V appears as a correction to van't Hoff's law and hence will be small; we can use

[6] Coleman and Germann, J. Chem. Phys. **1**, 847 (1933).

[7] Baud, Bull. Soc. Chim. (4) **17**, 329 (1915); Van Laar and Lorenz, Zeits. f. anorg. Chemie **146**, 42 (1925); Heitler, Ann. d. Physik (4) **80**, 630 (1926); Hildebrand and Wood, J. Chem. Phys. **1**, 817 (1933); Coleman and Germann, reference 6.

[8] Biron, J. Russ. Phys.-Chem. Soc. **41**, 569 (1909).

[9] Lewis and Randall, *Thermodynamics*, p. 214.

here the approximation $1/V=\pi/RT$ and this gives upon rearranging

$$\pi(V-\beta)=RT.$$

We obtain Eq. (1) once again.

In order to determine the dependence of β upon T we will go back to the function $A(T)$. The theoretical investigations[7] indicate that A will be very nearly constant over moderate temperature ranges. Hildebrand[10] believes that whenever there are no orientations between the molecules of two substances when they are mixed to form the solution, then A will be a constant. We do not believe that $\overline{H}_1-H_1^0$, can ever be *strictly* independent of temperature, except in the trivial case of ideal solutions. We believe that when we pass by a series of continuous states from a liquid solution to a gaseous solution (which is ideal or can be made so by an increase in its temperature), $\overline{H}_1-H_1^0$ should ultimately approach zero. This is not possible if A is strictly independent of temperature. (See reference 6). It seems therefore that although we can ordinarily assume A to be *approximately* constant, we must proceed with caution especially in cases where we suspect large orienting effects.

If A is a constant then from (16) we have

$$B=-A$$

and from (18)

$$\beta=-A\bar{v}_1/RT+\bar{v}_2-\bar{v}_1/2. \tag{19}$$

We see that as far as the form of this equation is concerned it is in harmony with the older theory in both its original form (Eq. (7)) and its modified form (Eq. (11)). Comparing Eqs. (11) and (19) we get the relations[11]

$$\phi=\bar{v}_2-\bar{v}_1/2, \tag{20}$$

$$A\bar{v}_1=\alpha. \tag{21}$$

In order to get Eq. (1) from (8) we dropped a small term $(\alpha/V^2)\phi$. We can proceed backwards and derive (8) from (1) by adding this same small term. Thus from Eq. (13), with A taken as constant over the temperature range considered, we can derive an osmotic pressure equation *having the same form as van der Waals gas equation*. However, such formal considerations can not, of course, give support to the interpretation of the constants concerned which is involved in Eqs. (20) and (21). Using Noyes' original treatment we get instead of (21) $A\bar{v}_1=\phi a$ and hence A must always be positive. This is not true.

It has not been the purpose of this paper to develop new equations but rather to give new meanings to old ones which already have received ample experimental confirmation; namely Eqs. (1) and (13).[12] We have tried to show that the van't Hoff analogy can be extended in the way originated by Noyes and Bredig, and that this extension agrees with modern developments.

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[10] Hildebrand, J. Am. Chem. Soc. **51**, 66 (1929).

[11] It will be of interest to consider the second of these equations in connection with the treatment of this problem given by Bancroft and Davis (J. Phys. Chem. **32**, 1 (1928)). They calculate the osmotic pressures of benzene and toluene in solutions composed of these two substances, *assuming them to be ideal*. They then show that these calculated pressures can be fitted by an equation of the van der Waals type over a *surprisingly large* range of compositions. But for the osmotic pressure of the benzene they used

$$\alpha=0.79198 \text{ atmos.}-(\text{liters})^2$$

and for the osmotic pressure of the toluene

$$\alpha=0.8338 \text{ atmos.}-(\text{liters})^2.$$

(We are using our own notation.) These values give (assuming $\bar{v}_1=v_1^0$)

$$A=7.3 \text{ liter-atmos.}=0.74 \text{ kilojoules}$$

and

$$A=9.3 \text{ liter-atmos.}=0.94 \text{ kilojoules.}$$

But in an *ideal* solution A must vanish and a comparison with the table given in reference 6 shows that these values are much too large to be negligible. These values are, as a matter of fact, much larger than the actual value of A which is (reference 6) 0.298 kilojoules. (A is identical with the α_2 given in the table in this case.) The ideal solution is, according to our treatment, the only case in which the complete van der Waals equation is not necessary—in this case alone does the equation degenerate into one exactly analogous to Hirn's gas equation, $p(V-b)=RT$.

[12] Besides the references cited, see Hildebrand (reference 10) for indirect confirmation of this equation with A considered as a constant.

Note on Electric Moments and Infrared Spectra, and the Structure of CO

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The desirability of measurements of infrared intensities in order to determine electric moments as functions of interatomic distances is illustrated by a discussion of available data on HCl, HI, CO and H_2O. Some new information on the structure of CO is obtained.

LITTLE attention seems usually to be paid to the limitations imposed by the fact that the ordinary data on electric moments, and the relations and conclusions therefrom, refer exclusively to molecules in their equilibrium configurations. The electric moment μ for each molecule or bond is known just for one particular value of the distance r between the atoms concerned. A deeper understanding of electric moments should result if we knew μ as a function of r over a range of r values for a number of different important bonds. Experimental data helping us to construct such curves can be obtained from measurements of the total-intensities of infrared vibration bands; theoretical relations between $\mu(r)$ curves and intensity data have been developed especially by Dunham.[1, 2, 3] Unfortunately such data are at present very scanty.[3a]

The few available data indicate interesting situations. We may consider first the hydrogen halides. In the case of HCl, which has been carefully discussed by Dunham,[1] infrared intensity measurements give information as to the variation of μ with r.[2] The result,[1] for r near r_e, is probably

$$\mu_{HCl}\times 10^{18}=1.03\pm(1.06\xi+0.07\xi^2), \qquad (1)$$

where $\xi=(r-r_e)/r_e$, with $r_e=1.276\times 10^{-8}$ cm. The intensity data cannot show whether the coefficients of ξ and ξ^2 are positive or negative, but the signs may be capable of determination by systematic considerations. The coefficient of ξ^2, it should also be noted, is obtained by solving a quadratic equation which gives 4.56 as a possible alternative to 0.07 in Eq. (1), but other considerations make this solution improbable. The experimental error in determining the coefficient of ξ^2 is really greater than 0.07, so we may say that this coefficient is zero (unless it should be 4.56) within experimental error.

Taking Eq. (1) as correct, and knowing that $\mu=0$ for $r=0$ and $r=\infty$, we can roughly sketch μ as a function of r (cf. Figs. 1a, 1b). The behavior of the curves near $r=0$ is not certain; the forms assumed in Figs. 1a, 1b correspond to the existence of a maximum value, at some finite $r>0$, for the effective charge q, where $\mu=qr$. [It may be, however, that q actually (for some molecules at any rate) rises asymptotically to a maximum at $r=0$. In this case the $\mu(r)$ curves should be given a finite slope at $r=0$.] With the foregoing and the very probable assumption that the $\mu(r)$ curve for HCl has only one maximum, its form is fairly well determined for each sign in Eq. (1). [It the coefficient of ξ^2 should be 4.56, the curve would go up with increasing steepness for $r>r_e$ in Fig. 1a, to a high maximum; in Fig.

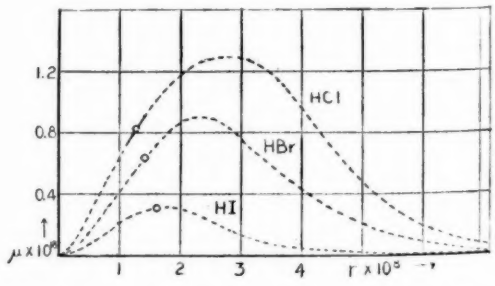

FIG. 1a. More probable forms of $U(r)$ curves (positive sign in Eq. (1)).

[1] J. L. Dunham, Phys. Rev. **35**, 1347 (1930).

[2] D. C. Bourgin, Phys. Rev. **29**, 794 (1927); J. L. Dunham, Phys. Rev. **34**, 438 (1929).

[3] L. Matheson, Phys. Rev. **40**, 813 (1932).

[3a] In the writer's opinion, the serious discrepancies noted by Van Vleck (*Theory of Electric and Magnetic Susceptibilities*, Oxford, 1932, pp. 45–70) between "atomic polarization" data and infrared vibration-rotation band intensities may probably be attributed to gross inaccuracy in the early infrared intensity measurements and to experimental errors in other data (cf. Van Vleck, pp. 52, 68). A very serious discrepancy between observed intensities of pure rotation bands of HCl and those predicted from $\mu(r_e)$ remains.

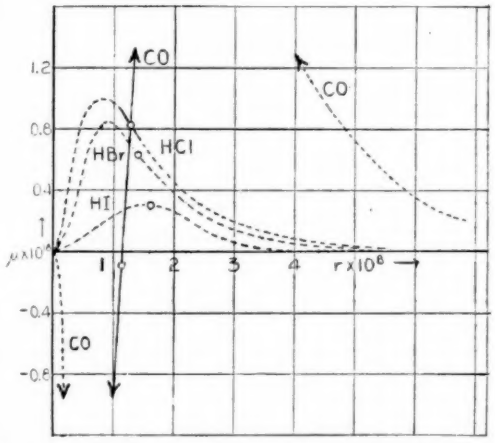

FIG. 1b. Negative sign in Eqs. (1), (3): less probable $U(r)$ curves for HCl, HBr, HI, most probable curve for CO.

1b it would descend with increasing steepness for $r>r_e$.]

No quantitative measurements on HBr or HI are available, but the extreme weakness[4] of the fundamental vibration band of HI ($v=0\rightarrow1$) shows that the coefficient of ξ must be very small, hence that μ must have a maximum near $r=r_e$. This, together with the result $\mu=0.38\times10^{-18}$ for $r=r_e=1.617\times10^{-8}$ cm, allows us to sketch the curve shown in Fig. 1. For HBr the $0\rightarrow1$ band is known to be much stronger than that for HI, although nothing quantitative is known. Knowing $\mu=0.79\times10^{-18}$ for $r=r_e=1.411\times10^{-8}$ cm for HBr, we may plausibly interpolate between HCl and HI to get the curve shown in Fig. 1a or Fig. 1b.

Fig. 1a corresponds to a maximum of q at r slightly less than r_e in the case of HI, at r slightly greater than r_e in the case of HCl. For Fig. 1b, the maximum of q for HCl comes at r considerably less than r_e; the HI curve is unchanged. It is not obvious which of these possibilities is correct.[5] Two other possible curves, based on 4.56 as the coefficient of ξ^2 in Eq. (1), are less probable, but cannot be absolutely ruled out without further evidence. Even with these ambiguities, the curves show interesting changes in the series HCl, HBr, HI.

[4] M. Czerny, Zeits. f. Physik **44**, 254–5 (1927). The pure rotation band of HI, whose intensity should depend on $\mu(r_e)$, is not much weaker than that of HBr, in agreement with theory.

[5] The $U(r)$ curves given by L. Pauling, J. Am. Chem. Soc. **54**, 998 (1932), are of interest in this connection.

For CO, infrared intensity measurements[3] combined with the values of $\mu(r_e)$ yield, for r near r_e ($r_e=1.15\times10^{-8}$):

$$\mu_{CO}\times10^{18}=0.118\pm(9.1\xi+3.7\xi^2 \text{ or } -3.4\xi^2) \quad (2)$$

In this case it is clear that, whether we use $+9.1\xi$ or -9.1ξ in Eq. (10), μ must reverse its sign very close to $r=r_e$. This can be understood if we assume an electronic structure for CO similar to that suggested by Pauling[5] (wave function ψ a mixture of $C^-\equiv O^+$ and $C=O$), but with the addition of a component C^+-O^- to ψ. [It may be noted that the structure given in terms of molecular orbitals by Hund and the writer is also equivalent to a linear combination of C^-O^+, CO, C^+O^- etc.] For small r, polarity C^-O^+ may reasonably be expected, since $C^-\equiv O^+$ should there be at its strongest.[5] For large r, polarity C^+O^- is expected, since C^++O^- then has considerably lower energy than C^-+O^+. Actually, it seems, C^-O^+ and C^+O^- must appear with about equal weight in ψ for $r=r_e$, and the struggle between them must be very keen there. The $\mu(r)$ curve shows that one of the two forms, in all probability C^-O^+, predominates decisively for small r, beginning with r not much less than r_e, and the other for r not much greater.[6] Assuming C^-O^+ dominant for small r, and calling μ negative for C^-O^+, the signs in Eq. (2) must be chosen as follows:

$$\mu_{CO}\times10^{18}=\mp0.118+9.1\xi+3.7\xi^2. \quad (3)$$

The alternative $-3.4\xi^2$ appears improbable. The only ambiguity remaining is then in the two possibilities ∓0.118, which is so small that it does not matter much. The -0.118 choice is shown in Fig. 1b.

The foregoing examples indicate the desirability of further quantitative measurements of in-

[6] Evidently the $U(r)$ curve for C^++O^- comes about equally as low as that for C^-+O^+ for r near r_e. Pauling (reference 5, Fig. 7) considers only the C^-O^+ curve. Probably the electron affinity of carbon is less than Pauling's estimate, so that the C^-O^+ curve is not as low as he supposed, and the C^+O^- curve therefore relatively lower. It is here supposed, contrary to Pauling, that the neutral $C=O$ component of ψ does not make an important contribution to μ (a small contribution, of polarity C^+O^-, may, however, be present in spite of the homopolar character of the bond, because of the unequal size of the two atoms).

frared intensities. Attention may be called to the possibility of interesting results with polyatomic as well as diatomic molecules. For example, although H_2O is known to have a large permanent electric moment, available data on its infrared absorption bands[7] indicate that terms analogous to the coefficient of ξ in Eq. (1) are relatively small. That is, μ_z, the component of the electric moment in the direction of the symmetry axis, is apparently near a maximum just as in HI, as regards symmetrical vibrations of the molecule: only a few weak bands are observed which correspond to an electric moment varying in the z direction (Δv_3= even). For those infrared bands (Δv_3= odd, where v_3 is the quantum number associated with the normal coordinate corresponding to asymmetrical vibrations) whose intensity depends on a moment (μ_y) perpendicular to the symmetry axis, the intensities are high, indicating that for μ_y the coefficient analogous to that of ξ in Eq. (1) is high.[8] For a non-vibrating molecule, $\mu_y=0$, of course. The available data are unfortunately too qualitative in character to permit of a satisfactory interpretation in relation to the electronic structure of H_2O; such a correlation, it may be pointed out, should involve relations between the coefficients of the expansion for μ_y as a function of the normal coordinates, and those of the similar μ_z expansion.

[7] R. Mecke and collaborators: Zeits. f. Physik **81**, 313, 445, 465 (1933); Phys. Zeits. **33**, 833 (1932).

[8] The fact that bands with Δv_3= odd depend on μ_y, those with Δv_3= even on μ_z, is easily deduced by group theory methods (procedure of L. Tisza, Zeits. f. Physik **82**, 48 (1933)). Cf. also W. Weizel, Zeits. f. Physik **88**, 214 (1934).

Raman Spectrum of Carbon Disulphide

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The Raman spectrum of liquid carbon disulphide has been investigated with high dispersion. In addition to the lines already known, five very faint lines have been observed. The intensities of the stronger lines were measured and, with a spectrograph of low dispersion, the degrees of depolarization of the two principal bands were determined. The results are in accord with the assumption made by Fermi, Dennison and Placzek that large perturbations of some of the energy levels occur on account of the approximate coincidence of ν_1 with $2\nu_2$. The values $\Delta=-120$ cm^{-1} and $|P|=17.8$ cm^{-1} are obtained for the difference $\Delta=\nu_1-2\nu_2$ and for the coupling constant $P=\beta h^{\frac{1}{2}}/4\pi^2\mu_1^{\frac{1}{2}}\mu_2(\nu_1+2\nu_2)^{\frac{1}{2}}$.

THE Raman spectrum of carbon disulphide has been studied by a number of investigators. The earlier workers[1, 2, 3, 4] found a strong band near 656 cm^{-1} and a less intense band around 800 cm^{-1}. Krishnamurti[5] observed that the stronger of these two principal bands has a weak companion at 647 cm^{-1}. This was confirmed by Bhagavantam,[6] Matossi and Aderhold,[7] and Mesnage.[8] The latter, employing a spectrograph of high dispersion, resolved the 800 cm^{-1} band into a band at 796.3 cm^{-1} and a weaker companion at 810.9 cm^{-1}. Pienkowski[9]

[1] C. V. Raman and K. S. Krishnan, Nature **122**, 882 (1928).

[2] A. Petriakaln and J. Hochberg, Zeits. f. physik. Chemie **B3**, 217, 405 (1929).

[3] A. S. Ganesan and S. Ventekateswaran, Nature **124**, 57 (1929); Ind. J. Phys. **4**, 196 (1929).

[4] Cl. Schaefer, F. Matossi and H. Aderhold, Phys. Zeits. **30**, 581 (1929).

[5] P. Krishnamurti, Ind. J. Phys. **5**, 105 (1930).

[6] S. Bhagavantam, Ind. J. Phys. **5**, 35, 59 (1930); Nature **126**, 995 (1930); Phys. Rev. **39**, 1029 (1932).

[7] F. Matossi and H. Aderhold, Zeits. f. Physik **68**, 683 (1931).

[8] P. L. Mesnage, J. de Phys. et le Rad. **2**, 403 (1931).

[9] S. Pienkowski, Acta. Phys. Pol. **1**, 87 (1932).

determined the relative intensities of the principal bands, obtaining the ratio 3.1. The degree of depolarization of these bands has been measured by Bhagavantam,[6] Pienkowski,[9] Cabannes and Rousset,[10] and Ventekateswaran.[11] Hanle,[12] by observation on circular polarization, determined an upper limit for the depolarizations. Besides the afore-mentioned bands, three very feeble bands were observed by Bhagavantam[6] at 400 cm^{-1}, 1229 cm^{-1}, and 1577 cm^{-1}. The presence of the 400 cm^{-1} band has been confirmed by Ventekateswaran[11] who also determined its depolarization.

The smallness of the dipole moment of CS_2, as well as other evidence,[13] suggests that the carbon disulphide molecule is linear and symmetrical. This assumption was shown by Placzek[14] to form a suitable basis for the interpretation of the Raman spectrum and has been definitely confirmed by the recent work of Dennison and Wright[15] and Bailey and Cassie[16] on the infrared absorption spectrum.

In view of the simple structure of linear triatomic molecules, it seemed desirable to obtain as accurate and detailed data on their Raman spectra as possible. We have, therefore, reexamined the Raman spectra of several molecules of this not very numerous class. In the present paper the results obtained with carbon disulphide will be reported.

Frequency Shifts

The carbon disulphide ("Merck C.P."), after being purified by shaking with mercuric chloride and by fractional distillation, was illuminated by four glass mercury arcs, each 32 cm long and surrounded by a reflector of proper shape. A 6 mm thick layer of a solution of quinine sulphate in water was interposed between the mercury lamps and the tube containing the carbon disulphide.

The scattered spectrum was photographed with a four-prism glass spectrograph having a linear dispersion of 7A per mm at 4400A. Agfa Isochrome plates and a fine-grain developer were used. The exposure time varied between 20 and 48 hours. No observable photochemical decomposition of the carbon disulphide occurred.

The measured frequency shifts are listed in the first column of Table I. All frequency shifts were observed as Raman lines excited by the 4358A mercury line. The most intense shifts were observed also as produced by the mercury lines 4348A, 4916A and 5461A, and as anti-Stokesian lines due to 4358A. The values found for the shifts 656.5 cm^{-1} and 796.0 cm^{-1} should be accurate to ± 0.5 cm^{-1}. Because of their proximity to the strong lines and to their lower intensity, the accuracy in the measurement of the satellites is somewhat smaller. The three very faint lines in the neighborhood of 400 cm^{-1} are probably measured correctly to ± 3 cm^{-1}. The observation of these lines was difficult because of the presence of a continuous background which was not entirely removed even after repeated purification of the carbon disulphide.

The frequencies 656.5 cm^{-1} and 796.0 cm^{-1} agree well with the measurements of previous observers but should be more accurate. The frequency 648.3 cm^{-1}, while in good accord with the value 647 cm^{-1} reported by Krishnamurti, differs markedly from the value 642.6 cm^{-1} found by Mesnage. There is a similar discrepancy between the frequency 810.9 cm^{-1} reported by

Table I.

Raman frequency	Intensity	Depolarization	Transition	Infrared frequency
383 cm^{-1}	—			389.4 cm^{-1}
395	0.05	0.8*	(0000)→(010±1)	396.8
403	—			405.8
640.9	—			
648.3	4.2		(010±1)→{(110±1)(030±1)}	
656.5	18.9	0.15	(0000)→{(1000)(0200)}	645
787.7	0.1			
796.0	1.5	0.18	(0000)→{(0200)(1000)}	807
804.9	0.5		(010±1)→{(030±1)(110±1)}	
812.6	0.1			
			(0000)→(0010)	1523

* Determined by S. Ventekateswaran (reference 11).

[10] J. Cabannes and A. Rousset, Ann. de Physique **19**, 229 (1933).

[11] S. Ventekateswaran, Phil. Mag. **15**, 263 (1933).

[12] W. Hanle, Ann. d. Physik **15**, 345 (1932).

[13] Cf. P. N. Gosh and P. C. Mahanti, Phys. Zeits. **30**, 531 (1929).

[14] G. Placzek, Zeits. f. Physik **70**, 84 (1931).

[15] D. M. Dennison and N. Wright, Phys. Rev. **38**, 2077 (1931).

[16] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. **A132**, 236 (1931); **A140**, 605 (1933).

Mesnage and our value 804.9 cm^{-1}. We were unable, even with long exposures, to confirm the lines 1229 cm^{-1} and 1577 cm^{-1} reported by Bhagavantam.

Intensities

It is a very difficult problem to measure the relative intensities of Raman bands. In most cases the rotational structure of the bands is not resolved well enough to separate the *Q*-branch completely from the rotational branches, and this may lead to serious error, especially when the Raman bands differ greatly in structure. To reduce this error, a spectrograph of high dispersion should be employed. Indeed, even with such an instrument, it will generally be necessary to use a considerably narrower slit than is ordinarily used when intensities of spectral lines are measured. This has the disadvantage that the peaks in the photometer record do not have the flat tops desirable for accurate measurement of the photographic blackening. Another source of error is the continuous background, so often present, which reduces the accuracy with which weak bands may be measured.

The Raman bands of carbon disulphide excited by the 4358A mercury line lie in a spectral region in which the variation with wave-length of the photographic sensitivity is very small. In addition, the principal bands lie rather close together. Hence, the methods of homogeneous spectrophotometry may be employed. The scattered spectrum was photographed with the previously mentioned four-prism spectrograph. The slit was 0.03 mm wide, the focal lengths of collimator and camera objectives being 50 cm and 75 cm, respectively. Intensity marks were put on the plate by means of a continuous light source and a step-weakener with six steps which had been calibrated by the aid of a Nuttall colorimeter. The step-weakener was placed on the axis of the collimator of the spectrograph about 1.5 m from the slit, and an image of it was formed on the slit. The light bulb serving as the source of continuous light was enclosed in a box having a window of variable size. A plate of white alabaster glass was placed between step-weakener and light bulb, and the intensity of illumination was adjusted so that the same exposure time could be used in photographing the intensity marks and the Raman spectrum. The photographic blackening was measured with a Moll, Type A, microphotometer, the slit in front of the thermoelement having in most cases a width of 0.10 mm. Fig. 1 shows a typical photometer record of the principal bands together with a reproduction to the same scale of the spectrum. The corresponding energy distribution is plotted in Fig. 2a and Fig. 2b, the curve for the weaker of the two principal bands being drawn to ten times as large a scale as that for the stronger band. The correction for the continuous background amounted to 17 percent of the maximum intensity in the case of the former curve, while it was less than one percent of the maximum intensity in the case of the latter curve.

The curves show a considerable difference in the structure of the two bands, and the question arises whether this difference is real, or whether it may be the result of experimental errors. We have made photometer records of three plates and have varied the speed of motion of the plate as well as other details of the procedure but have always obtained practically the same results. Furthermore, the difference in the shape of the curves cannot be explained by an error in the correction for the continuous background. For, the error required to reduce the two curves to approximately the same shape would have to be more than 200 percent of the computed correction. We must conclude, therefore, that the difference in the structure of the two bands is real.

The energy distribution curves indicate beyond doubt that each group of bands consists of more than two bands. We have attempted to analyze the groups into component bands, as indicated by the dotted curves in Fig. 2. This anslysis is to some extent arbitrary, especially in the case of the weaker group, and the accuracy is not great. It is now a question how the curves, obtained in the manner described, may be used for determining the relative intensities of the bands. The values listed in the second column of Table I are simply the maximum ordinates of each of the dotted peaks. If we assume that these values represent the relative intensities, we find the value 12.7 for the ratio between the intensities of the 656.5 cm^{-1} and 796.0 cm^{-1} bands. On the other hand, if we assume that the intensities are represented by the areas under the curves, we

R 151 CS_2 III

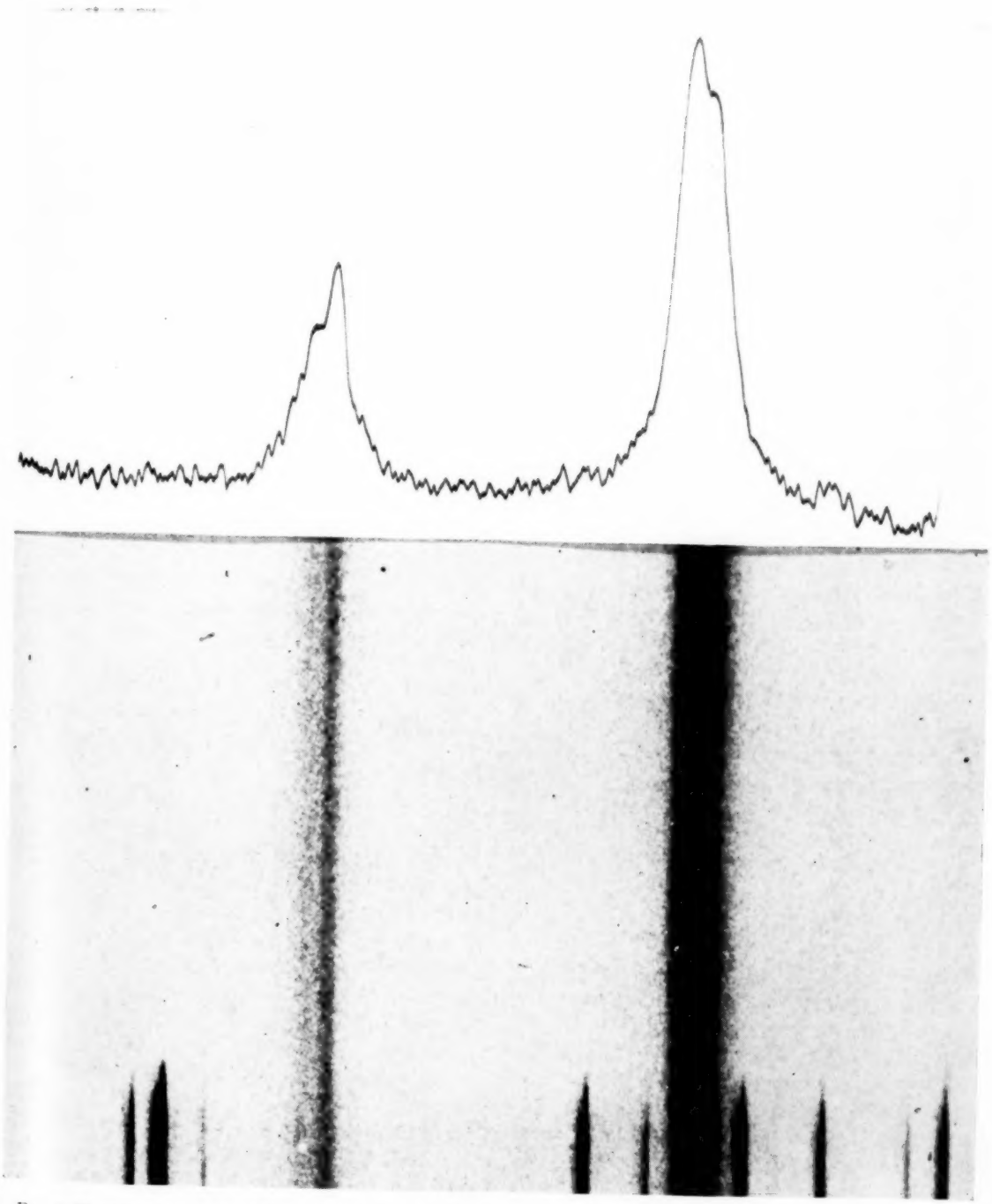

FIG. 1. Photometer record and reproduction of the principal Raman bands of carbon disulphide. *R* 151, CS_2 III.

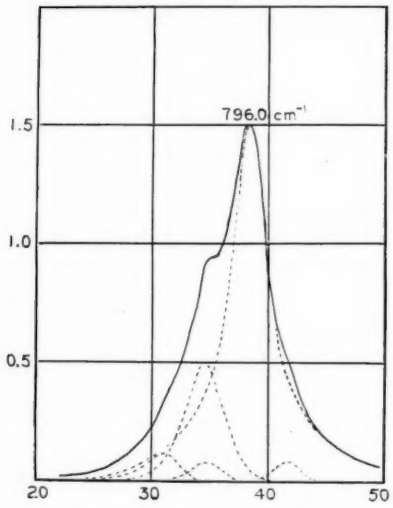

FIG. 2a.

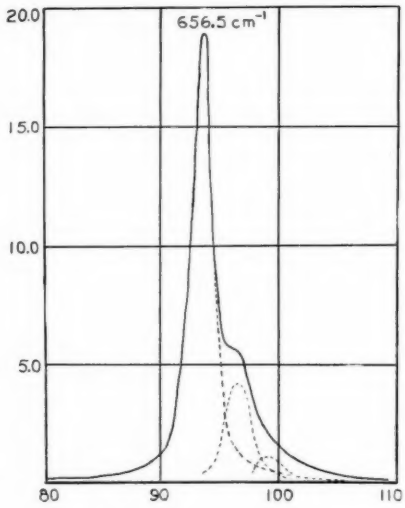

FIG. 2b.

FIG. 2. Energy distribution in the principal Raman bands of carbon disulphide.

get for the intensity ratio the value 3.0 which is in excellent agreement with the value 3.1 reported by Pienkowski. Unfortunately, Pienkowski does not give complete information regarding experimental details, so it is uncertain what weight should be attached to this agreement. It may be concluded from our curves with reasonable certainty that a measurement made in the usual way with a spectrograph of low dispersion will give a value in the neighborhood of 3.0 for the ratio of the intensities of the 656.5 cm^{-1} and the 796.0 cm^{-1} bands whereas a similar measurement with an instrument of high dispersion will yield a value as high as 12.7, or even slightly higher. We assume, therefore, that the latter value represents fairly well the true intensity ratio of the Q-branches.

A rough verification of this assumption may be obtained as follows. As indicated in Table I, the satellites 648.3 cm^{-1} and 804.9 cm^{-1} are due to transitions similar to those giving rise to the principal bands, the only difference being that the scattering molecules are in the excited (010 ± 1)-state rather than in the state of lowest energy. Hence, it is possible to compute the ratio between the intensities of the principal band and its satellite. Taking into account the double statistical weight of the (010 ± 1)-state, and assuming that the temperature is 300°K, we find the value 3.37. The ratios derived from the intensities listed in Table I, namely 4.5 and 3.0, are in fair agreement with this value.

The depolarization measurements described below, which were made with a spectrograph of low dispersion, lead to a determination of the ratio between the intensities of the 656 cm^{-1} and 796 cm^{-1} groups of bands. The average value found is 8.3 ± 0.3. The fact that this is considerably lower than the value 12.7 is undoubtedly a consequence of the smaller dispersion used in the polarization measurements.

POLARIZATION

The difficulties met with in intensity measurements are magnified when one turns to the problem of measuring the degree of depolarization of Raman lines. Since the incident light must have a well-defined direction in polarization experiments, only a small part of the light emitted by the source can be utilized for illumination. Hence, the scattered light will be very weak and this makes necessary the use of a fast spectrograph which will, generally, have a low dispersion. It will not always be possible, therefore, to separate the Q-branch completely from the rotational branches, and this may cause serious error on account of the large difference usually existing between the polarization of the rotational branches and that of the Q-branch. The extent to which the Q-branch is separated

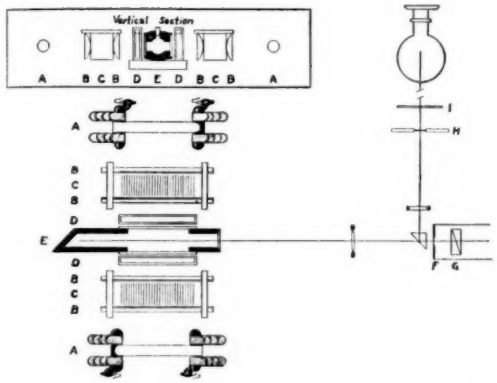

FIG. 3. Experimental arrangement for polarization measurements. *A*, Hg lamp; *B*, cylindrical lens; *C*, screens; *D*, filter; *E*, Raman tube; *F*, spectrograph slit; *G*, Wollaston prism; *H*, step-weakener; *I*, alabaster glass.

from the rotational branches and, hence, the observed depolarization will depend upon the width of the spectrograph slit. Usually, one cannot at the same time use a slit narrow enough to get the greatest possible resolution and wide enough to attain the maximum accuracy in the photometry.

The experimental arrangement used for measuring the degree of depolarization of the principal Raman lines of carbon disulphide is shown in Fig. 3. The liquid was contained in a suitably constructed porcelain tube *E* with black glazing on the inside surface and with cemented glass windows. Two 220-volt quartz mercury lamps *AA*, placed on opposite sides of the container, served as the sources of illumination. In order to reduce the continuous emission, the series resistances were increased to three times their normal value. The direction of the incident light should be perpendicular to the axis of the collimator and to the slit of the spectrograph. As has been shown by Ramakrishna Rao,[17] however, when the light source is of small extension and the proper precautions are taken, a lens may be used for focussing the light upon the scattering substance, thus increasing greatly the intensity of illumination. This fact was utilized in the following manner. Between each mercury lamp and the container were mounted two plano-cylindrical lenses *BB* which focussed the axis of the lamp at the axis of the container. Care was taken that lamps and lenses were accurately parallel to the collimator of the spectrograph and in the proper height. Between the lenses forming a pair were placed a series of blackened screens, 5 cm wide and 5 mm apart, which prevented the light not approximately at right angles to the collimator axis from reaching the container. Before entering the carbon disulphide, the light was filtered through a solution *DD* of 1 g meta-dinitrobenzene in 100 cm^3 carbon tetrachloride. This filter, which has been proposed by Bär,[18] removes the 4046A and 4078A mercury lines without absorbing the 4358A line appreciably.

The spectrograph had a collimator lens of 60 mm clear aperture and 60 cm focal length. The dispersive system consisted of a 65° hollow prism filled with ethyl cinnamate, the glass windows being large enough to transmit the entire beam of light. The camera lens was a Tessar of diameter 60 cm and focal length 21 cm. A quartz Wollaston prism was placed in the collimator tube 3 cm behind the slit with its refracting edges accurately parallel to the slit. Each spectral line was thus split up into two components lying side by side, one being polarized parallel and the other at right angles to the slit. Apart from the correction for the polarization produced by the refraction in the prism, the ratio between the intensity of the latter component to that of the former is equal to the degree of depolarization. Intensity marks were put on the plate by means of a step-weakener *H* illuminated by a continuous light source, the light passing through a plate *I* of alabaster glass. An image of the step-weakener was formed on the slit by means of an achromatic lens and a totally reflecting prism. The correction for the polarization produced by the prism was determined by letting unpolarized light from a Geissler tube containing helium enter the spectrograph and measuring the relative intensities of the perpendicular and parallel components. The correction varied only slightly with wavelength and amounted to 36 percent for the principal Raman lines excited by 4358A. The width of the spectrograph slit was either 0.05 mm or 0.10 mm, essentially the same value being obtained for the depolarization in both cases.

[17] J. Ramakrishna Rao, Ind. J. Phys. **2**, 61 (1927).

[18] R. Bär, Helv. Phys. Acta. **5**, 174 (1932).

The exposure time varied between $1\frac{3}{4}$ and 4 hours.

Under these conditions, the band at 648.3 cm^{-1} is not separated from the principal band at 656.5 cm^{-1}, and the satellite at 804.9 cm^{-1} is fused with the principal band at 796.0 cm^{-1}. Also, the Q-branches are not completely separated from the rotational branches.

The values obtained for the degree of depolarization ρ_n (the subscript n indicating that the incident light was unpolarized) are listed in the third column of Table I. These values could be duplicated to within 5 percent. Because of the imperfect resolution, however, they are undoubtedly somewhat higher than the true depolarizations of the Q-branches of the 656.5 cm^{-1} and 796.0 cm^{-1} bands. On the other hand, the depolarizations, 0.13 and 0.18, found by us are considerably lower than those found by previous observers. Indeed, Pienkowski[9] found 0.27 and 0.29 for the 656.5 cm^{-1} and 796.0 cm^{-1} bands, respectively. Bhagavantam,[6] and also Cabannes and Rousset,[10] found the value 0.25, and Ventekateswaran[11] the value 0.2, for both lines. Only Cabannes and Rousset give sufficient experimental detail to permit of an estimate as to the reason for the difference between their results and ours. While this difference cannot arise from the fact that the incident light was somewhat less accurately parallel in their experimental arrangement than in ours, it may be due to their using a spectrograph slit four times as wide as the widest slit used by us.

Discussion of Results

A linear and symmetrical triatomic molecule will, in general, have only one strong Raman band.[14] The presence of two nearly equally intense bands in the Raman spectrum of carbon dioxide was explained by Fermi[19] as the result of an abnormally large perturbation arising from the approximate coincidence of ν_1 with $2\nu_2$. In the Raman spectrum of carbon disulphide, there are also two strong bands, which, however, differ much more in intensity than do the two strong CO_2-bands, and it has been suggested by Fermi that the same accidental degeneracy, although not as complete, occurs in the CS_2-molecule as in CO_2. The theory has been worked out in greater detail by Dennison[20] and by Placzek[21] and these authors have also discussed the experimental evidence.[22]

Our results are in good accord with this view regarding the origin of the principal Raman bands of CS_2. In the fourth column of Table I are indicated the transitions assumed to give rise to the stronger bands. The vibrational states are characterized by the quantum numbers V_1, V_2, V_3, and i, introduced by Dennison.[23] The symbols $\{(1000)(0200)\}$ and $\{(0200)(1000)\}$ are used to represent the states produced by partial fusion of the (1000)- and (0200)-states, the component having the largest numerical factor in the resulting wave function being written first. The symbols $\{(110\pm1)(030\pm1)\}$ and $\{(030\pm1)(110\pm1)\}$ have similar meanings.

In the last column of Table I are listed the frequencies determined from the infrared absorption spectrum. The three frequencies in the neighborhood of 400 cm^{-1} were measured by Dennison and Wright,[15] and the other frequencies are obtained from the measurements of Bailey and Cassie.[16] The agreement between the Raman and infrared frequencies is satisfactory when the experimental errors and the fact that the infrared frequencies were obtained with CS_2 in the gaseous form are taken into consideration.

If we assume that the perturbation term βqr^2 produces an effect which is large compared with that of all other perturbation terms, we may use the measured frequencies of the principal Raman bands and their satellites to compute the difference $\Delta=\nu_1-2\nu_2$, the frequency ν_2, and the numerical value of the quantity

$$P=\beta h^{\frac{1}{2}}/4\pi^2\mu_1^{\frac{1}{2}}\mu_2(\nu_1+2\nu_2)^{\frac{1}{2}}$$

where μ_1 and μ_2 are the reduced masses associated with the vibrations ν_1 and ν_2, respectively.[24]

[19] Fermi, Zeits. f. Physik **71**, 250 (1931).

[20] D. M. Dennison, Phys. Rev. **41**, 304 (1932).

[21] G. Placzek, *Rayleigh-Streuung und Raman-Effekt*, Marx: Handbuch der Radiologie, 2nd ed., Vol. 4, Part II. We are indebted to Dr. Placzek for the opportunity of seeing this article before its publication.

[22] Cf. also A. B. D. Cassie and C. R. Bailey, Zeits. f. Physik **79**, 35 (1932).

[23] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1930).

[24] Cf. Reference 21, pp. 324–325.

In fact, we have

$$(\Delta^2+16P^2)^{\frac{1}{2}}=796.0-656.5=139.5\ \text{cm}^{-1},$$

$$(\Delta^2+32P^2)^{\frac{1}{2}}=804.9-648.3=156.6\ \text{cm}^{-1},$$

and

$$\nu_1+2\nu_2 \leqq 796.0+656.5 \leqq 804.9+648.3 \leqq 1452.8\ \text{cm}^{-1}.$$

Solving these equations, we obtain

$$\Delta=-120\ \text{cm}^{-1},\ |P|=17.8\ \text{cm}^{-1},\ \nu_2=393.2\ \text{cm}^{-1}.$$

The agreement between the computed and the observed values of ν_2 is very satisfactory. The values for Δ and $|P|$ are more satisfactory than the values $\Delta=-136.7$ cm^{-1} and $|P|=7.0$ cm^{-1} computed by Dennison[20] from Krishnamurti's measurements of the principal Raman bands and the value ν_2 determined by Dennison and Wright in the infrared absorption. Also, the values for Δ, $|P|$, and ν_2, derived from our measurements should be more accurate than the values $\Delta=106$ cm^{-1}, $|P|=33$ cm^{-1}, and $\nu_2=389.5$ cm^{-1}, computed by Placzek[21] from the data of Mesnage.

If it be assumed that the matrix elements $\alpha_1=(0000|\alpha|1000)$ and $\alpha_2=(0000|\alpha|0200)$ of the polarizability tensor have approximately the same relative anisotropy, it is possible,[25] from the measured ratio between the intensities of the 656.5 cm^{-1} and 796.0 cm^{-1} bands and the value of Δ, to estimate the value of the quantity $|\alpha_1/\alpha_2|^2$ which would represent the ratio between the probabilities of the transitions (0000) $\rightarrow$(1000) and (0000) $\rightarrow$(0200) if no accidental degeneracy were present. Taking the value 12.7 for the intensity ratio, we find $|\alpha_1/\alpha_2|^2=40{,}000$, a value which is of the order of magnitude to be expected.

From the interpretation of the bands, one would expect the depolarization of the 656.5 cm^{-1} band to be smaller than that of the 796.0 cm^{-1} band, and also both depolarizations to be small. The measured values are in good accord with this expectation. However, until the depolarizations have been measured for the principal lines and the satellites separately, it is impossible to draw quantitative conclusions.

It is an interesting fact that the band (0000)$\rightarrow$(010$\pm$1), which is forbidden in the Raman spectrum on account of the antisymmetry of the ν_2-vibration, is observed, although with low intensity. The presence of this band is undoubtedly connected with the fact that the carbon disulphide has been studied in the liquid rather than in the gaseous form. The depolarization 0.8 found by Ventekateswaran for this band is in good agreement with the value 6/7 to be expected from theory. The very faint and broad lines 383 cm^{-1} and 403 cm^{-1} probably represent the maxima of unresolved rotational branches. Considering the low intensity, the frequencies are in fair agreement with those found by Dennison and Wright in the infrared.

The faint lines 640.9 cm^{-1}, 787.7 cm^{-1}, and 812.6 cm^{-1}, may be due to transitions from the excited levels {(1000)(0200)}, {(0200)(1000)}, and (020$\pm$2). An unambiguous interpretation is not possible, however, until we have a more complete knowledge of the vibrational levels of the CS_2-molecule.

[25] Cf. reference 21, p. 321.

Molecular Symmetry and the Reduction of the Secular Equation. Part II

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(Received April 28, 1934)

Symmetry is used to reduce exactly the secular equation for nine monovalent atoms forming a body-centered cube from an equation of forty-second degree to equations of third degree and lower. Application of the results is then made to calculate approximately the energy of the isolated unit cell for sodium. The vector method recently put forward by Van Vleck is shown to be a valuable check on such calculations.

IN an earlier communication[1] the application of group theory to the reduction of secular equations involving bond-eigenfunctions was outlined, and a number of examples were given to illustrate the method. This earlier communication will be referred to as Part I.* We here extend the method of Part I somewhat and consider the further example of eight monovalent atoms at the corners of a cube with a ninth atom at the cube center. The problem of the homogeneous formation of crystal nuclei of as many as eight metal atoms has been discussed previously.[2, 3] The present discussion is an extension that includes the unit cell of nine atoms, which, however, is still very different in properties from the metal in bulk. For the energy of large crystal aggregates various authors have obtained interesting results using very different methods from those here found useful.[4, 5]

THE GENERAL METHOD

We consider the nine valence electrons on nine monovalent atoms forming a body-centered cube. The uncrossed set of bond-eigenfunctions (the linearly independent set of Rumer) is the same as that for the ten electron problem if one orbital is moved to infinity. We therefore arrange the ten letters a to j alphabetically on a circle, and write down at once the 42 uncrossed bond-eigenfunctions, omitting the tenth orbital j in each case. 14 of these are like the singlet bond-eigenfunctions for the eight electron problem with, however, a ninth orbital i added, i.e., there are four bonds connecting the orbitals a to h in pairs, and no bond to the orbital i at the cube center. The other 28 bond-eigenfunctions have one bond involving the orbital i and may be regarded as arising from the 28 triplet states for eight electrons. Any of the symmetry operations which transform a cube into itself transforms the first 14 eigenfunctions into linear combinations which involve only those 14 eigenfunctions, and transforms the 28 eigenfunctions into linear combinations which involve only those 28. Consequently these two sets of uncrossed eigenfunctions may be reduced entirely separately.

The symmetry operations for the body-centered cube may be found by consideration of Fig. 1. There are three generating operations: rotation through 90° about an axis perpendicular to one face, say *dcef*; rotation through 90° about an axis perpendicular to another face, say *adfg*; and inversion. These three operations may be written, respectively, $R_1=(abhg)(dcef)$; $R_2=(adfg)(bceh)$; and $J=(ae)(bf)(cg)(dh)$. By successive multiplication of R_1 and R_2 we obtain altogether 24 operations which go into one another on continued multiplication. The well-

[1] H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. **1**, 777 (1933).

* The numbering of equations in Part I will be retained in this paper, so that the numbering of new equations will begin with (7). We should also like to call attention to the following errors in Part I: On p. 779, column 1, line 7 from bottom and column 2, line 13 from top, read *unlike* for *like;* column 2, line 18 from bottom, read $(-1)^p$ for $(-2)^p$; page 780, column 1, read χ_i' and χ_1' for χ_i and χ_1 where they appear by themselves. The matrix component in case II should have the opposite sign.

Note also the following errata in the communication by H. Eyring and G. E. Kimball to J. Chem. Phys. **1**, 626 (1933): The coefficients for the three classes should of course be Class I, $-\frac{1}{2}x$; Class II, $-2x$; Class III, $+x$.

[2] H. S. Taylor, H. Eyring and A. Sherman, J. Chem. Phys. **1**, 68 (1933).

[3] F. Seitz and A. Sherman, J. Chem. Phys. **2**, 11 (1934).

[4] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[5] O. K. Rice, J. Chem. Phys. **1**, 49 (1933). See also Hume-Rothery, *The Metallic State*, Oxford Press, 1934.

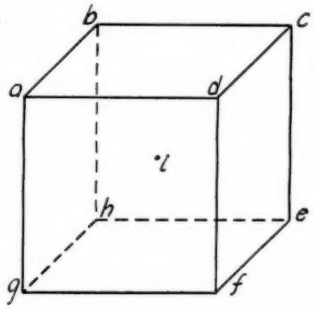

FIG. 1.

known group theoretical method for getting all operations belonging to the same class as the operation R_a is to form all products of the type $R_n \times R_a \times R_n^{-1} = R_b$, where R_n is taken successively as each operation of the group, and where of course $R_n \times R_n^{-1} = E$, the identity. These 24 operations are thus found to form five classes. Then by multiplying each of these 24 operations by the inversion J we obtain 24 more operations. Since $R_n \times J = J \times R_n$, we have at once the relationship $(J \times R_n) \times R_a \times (R_n^{-1} \times J) = R_n \times R_a \times R_n^{-1} = R_b$. Hence the introduction of J does not alter any of the original classes. Furthermore, since $R_n \times (J \times R_a) \times R_n^{-1} = J \times (R_n \times R_a \times R_n^{-1}) = J \times R_b$, the 24 new operations form five new classes each of which is found by multiplying the members of each of the original five classes by J. A representative of each class together with the number of operations in that class is given below:

Class	Representative	No.	Class	Representative	No.
C_1	Identity	1	$C_6 = J \times C_1$	Inversion	1
C_2	$(af)(be)(ch)(dg)$	3	$C_7 = J \times C_2$	$(ab)(cd)(ef)(gh)$	3
C_3	$(adfg)(bceh)$	6	$C_8 = J \times C_3$	$(ahfc)(bged)$	6
C_4	$(ae)(bf)(cd)(gh)$	6	$C_9 = J \times C_4$	$(ch)(dg)$	6
C_5	$(acf)(beg)$	8	$C_{10} = J \times C_5$	$(agfecb)(dh)$	8

This is one of the groups Bethe discussed in his important paper on term-splitting in crystals.[6]

We next obtain the characters χ_i' and χ_i of the reducible and of the irreducible representations, respectively, by application of the rules given in Part I. The method for obtaining χ_i may be shortened in the following way: One finds the characters for the subgroup formed by the first 24 operations (five classes and therefore five representations). Since the inversion commutes with all operations of the group, for every irreducible representation it is a diagonal matrix whose character is plus or minus that of the identity. Hence when the original subgroup is extended by the introduction of J and therefore of five new classes of operations, each of the original five representations gives rise to two representations (each with ten classes). In each new pair of representations, the characters of the five original classes remain unchanged; those of the five new classes are in one case unchanged and in the other multiplied by -1. This is at once clear from consideration of Table I.

TABLE I.

Class	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	n_{14}	n_{28}
Representation Γ_1	1	1	1	1	1	1	1	1	1	1	3	0
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1	0	0
Γ_3	2	2	0	0	−1	2	2	0	0	−1	2	0
Γ_4	3	−1	1	−1	0	3	−1	1	−1	0	0	2
Γ_5	3	−1	−1	1	0	3	−1	−1	1	0	1	2
Γ_6	1	1	1	1	1	−1	−1	−1	−1	−1	1	0
Γ_7	1	1	−1	−1	1	−1	−1	1	1	−1	0	2
Γ_8	2	2	0	0	−1	−2	−2	0	0	1	0	1
Γ_9	3	−1	1	−1	0	−3	1	−1	1	0	0	3
Γ_{10}	3	−1	−1	1	0	−3	1	1	−1	0	1	1
D_{14}	14	6	2	6	2	6	6	2	2	0		
D_{28}	28	−4	0	−4	1	−4	−4	0	4	−1		
h	1	3	6	6	8	1	3	6	6	8		

The number of times an irreducible representation having the character χ_i for the class C_i will appear in the reduced representation with the character χ_i' is given by the expression

$$n = \sum_i h_i \chi_i \chi_i' / N, \tag{5}$$

where N is the total number of operations (*viz.* 48) and h_i is the number of operations in C_i.

We now consider the uncrossed set of bond-eigenfunctions divided into two sets of 14 and 28 functions as mentioned above. The characters χ_i' may be found for each of these two sets independently. Then from (5) values of n may be obtained for each irreducible representation for both sets. In Table I the characters of the ten irreducible representations are given. The two columns marked n_{14} and n_{28} give the number of times each irreducible representation appears in the two divisions of the uncrossed set. The rows D_{14} and D_{28} give the characters for the sets of 14 and 28 bond-eigenfunctions, respectively. The row h gives the number of operations in each class.

[6] H. Bethe, Ann. d. Physik 3, 133 (1929).

If an irreducible representation appears p times, then it will be necessary to solve an equation of degree p to obtain the corresponding energy levels. Thus in the present problem the equation of highest degree is a cubic. The column C_1 gives of course the dimension of the irreducible representation. For example, one finds three eigenfunctions which are independent, each of which is a representation of Γ_1 and is a linear combination of the set of 14 bond-eigenfunctions only; but for Γ_5 there will be one three dimensional eigenfunction which is a linear combination of the set of 14 and two three dimensional eigenfunctions which are linear combinations of the set of 28. These two sets of uncrossed bond-eigenfunctions are non-combining, so that in the case of Γ_5 one linear and one quadratic equation must be solved instead of a cubic.

Calculation of the Energy Levels

Two methods will be described for obtaining the energy levels for a body-centered cube. In method I one obtains the eigenfunctions of the bases using the irreducible representations. In method II one uses the characters of the irreducible representations to find the energy levels without first finding the complete bases of the representations.

Method I

If one has the matrices corresponding to the operations for the irreducible representations, it is very easy to find the eigenfunctions having the symmetry of each representation in the following way.[7] Let $a_n{}^j$ be the element of the first row and first column of the reciprocal of the matrix for Γ_j which corresponds to the particular permutation R_n taken from our group of 48 operations. Let ψ_k be some one of the bond-eigenfunctions of the uncrossed set, and Ψ^j be the eigenfunction which we seek as part of the basis of the irreducible representation Γ_j. Now for any ψ_k we obtain a Ψ^j by forming the following sum

$$\Psi^j = \sum_{n=1}^{48} a_n{}^j R_n \psi_k. \tag{7}$$

It may happen that for a given ψ_k the Ψ^j so obtained is zero, but by trying enough ψ_k's, a complete set of the Ψ^j's can be obtained. It is also necessary to determine whether two such Ψ^j's are linearly independent or not. This may readily be done by expressing each in terms of the uncrossed set.

The method just outlined works very simply if the matrices of the irreducible representations are available. As soon as one of the eigenfunctions forming part of the basis for a particular irreducible representation (of higher dimension than the first) is found, the others can easily be found by examining the matrices to find an operation which transforms the known eigenfunction into a second one and carrying out this transformation.

If the matrices of the irreducible representations are not known, they may be obtained from the characters and from the multiplication table of the operations by a direct but often laborious algebraic procedure.

Method II

It is not necessary, however, to find these matrices, for the characters themselves can be used directly to obtain as many eigenfunctions as are required to calculate all the energies. We proceed exactly as in the method just described except that in Eq. (7) we replace $a_n{}^j$ by $\chi_n{}^j$, the character of the n-th matrix in the irreducible representation Γ_j. We therefore have the equation

$$\Phi^j = \sum_{n=1}^{48} \chi_n{}^j R_n \psi_k. \tag{8}$$

The eigenfunction Φ^j will be identical with Ψ^j (obtained by Method I) for one dimensional representations, but for any representation of dimension greater than one Φ^j will be the sum of the eigenfunctions which form the basis of that representation. Thus Φ^j will be as useful as Ψ^j in calculating the energies and will be much more readily obtainable in cases where the irreducible representations are not available.

To illustrate the usefulness of this method in calculating energies, let Φ_a and Φ_b be two eigenfunctions obtained in this way from two bond-eigenfunctions ψ_a and ψ_b for a given irreducible representation (of at least second degree). It is

[7] See E. Wigner, *Gruppentheorie* p. 123, Vieweg and Sohn, 1931. Also F. Seitz and A. Sherman, reference 3.

then necessary to evaluate the integral

$$I=\int \Phi_a H \Phi_b d\tau = \int \sum_{m=1}^{48} \chi_m R_m \psi_a H \sum_{n=1}^{48} \chi_n R_n \psi_b d\tau$$

$$= \int \psi_a H \sum_m \sum_n \psi_m R_m^{-1} \chi_n R_n \psi_b d\tau.$$

Since R_m and R_m^{-1} belong to the same class and therefore have the same character, we may write

$$I=\int \psi_a H \sum_m \sum_n \chi_m R_m \chi_n R_n \psi_b d\tau.$$

But

$$\sum_m \sum_n \chi_m R_m \chi_n R_n = \sum_i \sum_j \chi_i \chi_j C_i C_j = \sum_i \sum_j \chi_i \chi_j \sum_k c_{ijk} C_k$$

by Eq. (3). One finds that

$$\sum_i \sum_j \chi_i \chi_j \sum_k c_{ijk} C_k = N(\sum \chi_k C_k / \chi_1).$$

Hence

$$I=(N/\chi_1)\int \psi_a H \sum_k \chi_k C_k \psi_b d\tau$$

$$=(N/\chi_1)\int \psi_a H \Phi_b d\tau;$$

N/χ_1 is of course the same for all integrals in a given representation and may therefore be neglected. Hence in finding the matrix components between Φ_a and Φ_b one need only sum the matrix components between ψ_a, the first term of Φ_a, and each term $\chi_n R_n \psi_b$ of Φ_b.

Methods I and II are now applied to the determination of the energy levels associated, respectively, with the 14 and with the 28 bond-eigenfunctions of the uncrossed set. In the first case, the generating operations R_1 and R_2 for the irreducible representations are: for Γ_1 and Γ_6: 1, 1; for Γ_2 and Γ_7: -1, -1;

$$\text{for } \Gamma_3 \text{ and } \Gamma_8: \begin{vmatrix} -1 & 0 \\ -1 & 1 \end{vmatrix}, \quad \begin{vmatrix} 1 & -1 \\ 0 & -1 \end{vmatrix};$$

$$\text{for } \Gamma_4 \text{ and } \Gamma_9: \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix}, \quad \begin{vmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{vmatrix};$$

$$\text{for } \Gamma_5 \text{ and } \Gamma_{10}: \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{vmatrix}, \quad \begin{vmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{vmatrix}.$$

For Γ_1 to Γ_5 J is the same as the identity, while for the last five representations J is obtained from the identity by changing all signs. All other matrices are obtainable from the generating matrices by multiplication. If we make use of these representations and Eq. (7) in the manner described, we obtain 14 eigenfunctions distributed among the representations in the way indicated by the column n_{14} of Table I. They form the bases for three representations of Γ_1: $\psi_1 = ae\ bf\ cg\ dh\ i$; $\psi_2 = ab\ cd\ ef\ gh\ i + ag\ bh\ ce\ df\ i + ad\ bc\ eh\ fg\ i$; and $\psi_3 = ah\ bg\ cf\ de\ i + ac\ bd\ eg\ fh\ i + af\ be\ ch\ dg\ i$; two representations of Γ_3: $\psi_4 = ag\ bh\ ce\ df\ i - ab\ cd\ ef\ gh\ i$ with $\psi_5 = ag\ bh\ ce\ df\ i - ad\ bc\ eh\ fg\ i$; and $\psi_6 = ac\ bd\ eg\ fh\ i - af\ be\ ch\ dg\ i$ with $\psi_7 = ac\ bd\ eg\ fh\ i - ah\ bg\ de\ cf\ i$; one representation of Γ_5: $\psi_8 = ab\ ch\ dg\ fe\ i + af\ be\ cd\ gh\ i$ with $\psi_9 = ah\ bc\ ed\ fg\ i + ad\ bg\ cf\ eh\ i$ and with $\psi_{10} = ac\ bh\ df\ ge\ i + ag\ bd\ ce\ fh\ i$; one representation of Γ_6: $\psi_{11} = ac\ be\ dg\ fh\ i + af\ bg\ ch\ de\ i + ah\ bd\ cf\ ge\ i - af\ bd\ ch\ eg\ i - ah\ be\ cf\ dg\ i + ac\ bg\ de\ fh\ i$; and one representation of Γ_{10}: $\psi_{12} = ad\ bh\ ce\ fg\ i - ag\ bc\ df\ eh\ i$ with $\psi_{13} = ad\ bc\ ef\ gh\ i - ab\ cd\ eh\ fg\ i$ and with $\psi_{14} = ab\ cf\ de\ gh\ i - ah\ bg\ cd\ ef\ i$.

To obtain the corresponding energies we use the method of calculating matrix components described in Part I and previous papers. α is the interchange integral for two monovalent atoms at opposite ends of a cube edge; β for two atoms at opposite ends of a cube diagonal γ for two atoms at opposite ends of a cube diagonal; and δ the interchange integral for one atom at a corner and another at the center of the cube. Q is the sum of all potential energies which do not depend on the spin of the electrons, i.e., those due to coulombic attraction or to polarization of the type arising from second order perturbations. As usual multiple interchange integrals have been neglected. E_j is the total energy corresponding to Γ_j.

Using ψ_1, ψ_2 and ψ_3 we obtain, after normalization, the following cubic for the energy for Γ_1:

$$\begin{vmatrix} [(Q-E_1-4\delta)-6\alpha-6\beta+4\gamma] & 6(\alpha-\beta) & 0 \\ 6(\alpha-\beta) & [2(Q-E_1-4\delta)-16\beta] & (\alpha-\beta) \\ 0 & (\alpha-\beta) & {}^1/_{20}[(Q-E_1-4\delta)-2\alpha-2\beta-4\gamma] \end{vmatrix}=0.$$

With ψ_4 and ψ_6 we get for Γ_3 the two energies (each a double root): $E_3=Q-4\delta-4\alpha-2\beta-2\gamma \pm 2[(\alpha-\beta)^2+(\alpha-\gamma)^2]^{\frac{1}{2}}$. For Γ_5 we use ψ_8 and get the energy (a triple root): $E_5=Q-4\delta-4\alpha-4\beta$. For Γ_6 we use ψ_{11} and get the energy: $E_6=Q-4\delta-6\alpha-2\gamma$. For Γ_{10} we use ψ_{12} and get the energy (a triple root): $E_{10}=Q-4\delta-2\alpha-4\beta-2\gamma$.

We now consider the 28 bond-eigenfunctions and the corresponding energies obtained by method II. Only 11 eigenfunctions of the type given in Eq. (8) are obtained. These are sufficient to determine all energy levels because of the degeneracy. For if a particular representation is n-dimensional, there are n equal roots, and hence any linear combination of the n possible eigenfunctions is sufficient for the determination of these roots. As stated above, method II yields eigenfunctions which are the sum of the n eigenfunctions that would have been obtained by method I. The 11 eigenfunctions are the following: for Γ_4, $\Phi_1=\sum_n\chi_n{}^4R_n(ab\ c\ di\ eh\ fg)$ with $\Phi_2=\sum_n\chi_n{}^4R_n(ab\ c\ di\ ef\ gh)$; for Γ_5, $\Phi_3=\sum_n\chi_n{}^5R_n(ab\ c\ di\ ef\ gh)$ with $\Phi_4=\sum_n\chi_n{}^5R_n\times(a\ bg\ cf\ de\ hi)$; for Γ_7, $\Phi_5=\sum_n\chi_n{}^7R_n(ab\ c\ di\ ef\ gh)$ with $\Phi_6=\sum_n\chi_n{}^7R_n(af\ be\ cd\ g\ hi)$; for Γ_8, $\Phi_7=\sum_n\chi_n{}^8R_n(ab\ c\ di\ eh\ fg)$; for Γ_9, $\Phi_8=\sum_n\chi_n{}^9\times R_n(ab\ c\ di\ ef\ gh)$ with $\Phi_9=\sum_n\chi_n{}^9R_n(ab\ c\ dg\ ef\ hi)$ and with $\Phi_{10}=\sum_n\chi_n{}^9R_n(a\ bg\ cf\ de\ hi)$; and for Γ_{10}, $\Phi_{11}=\sum_n\chi_n{}^{10}R_n(a\ bg\ cf\ de\ hi)$.

The corresponding equations for the energies are: for Γ_4, $E_4=Q-2\delta-\frac{1}{3}(11\alpha+11\beta+8\gamma) \pm\frac{1}{6}[2(149\alpha^2+245\beta^2+20\gamma^2-374\alpha\beta+76\alpha\gamma-116\beta\gamma)]^{\frac{1}{2}}$, for Γ_5, $E_5=Q-2\delta-\frac{1}{24}[(x+8y) \pm[(x+8y)^2-32xy+200z^2]^{\frac{1}{2}}]$ where $x=56\alpha+29\beta+35\gamma$, $y=2\alpha+8\beta+5\gamma$, and $z=\alpha-2\beta+\gamma$ (each root a triple root); for Γ_7, $E_7=Q-2\delta-2\alpha-8\beta\pm 2[4(\alpha-\beta)^2+\gamma^2+\alpha\beta-\alpha\gamma-\beta\gamma]^{\frac{1}{2}}$; for Γ_8, $E_8=Q-2\delta-4\alpha-4\beta-2\gamma$ (a double root); for Γ_9, the three triple roots

$$\begin{vmatrix} [2(Q-E_9-2\delta)-8\alpha-10\beta-2\gamma] & 0 & 3(4\alpha-3\beta-\gamma) \\ 0 & [3(Q-E_9-2\delta)-10\alpha-10\beta-2\gamma] & -2\alpha-6\beta+8\gamma \\ 3(4\alpha-3\beta-\gamma) & -2\alpha-6\beta+8\gamma & \frac{1}{4}[87(Q-E_9-2\delta) \\ & & -574\alpha-240\beta-56\gamma] \end{vmatrix}=0$$

and for Γ_{10}, $E_{10}=Q-2\delta-6\alpha-2\beta-2\gamma$ (a triple root).

Energy for an Isolated Unit Cell of Sodium

In order to obtain an approximate picture of the energy levels for sodium we have estimated the integrals Q, α, β, γ and δ from a Morse curve using the constants $D=17.5$, $\omega_0=159$, $r_0=3.15$, and a corresponding value for a of 0.838. The coulombic integral was taken to be 28.3 percent of the total binding energy of the molecule in agreement with Rosen's calculations.[8] The additional binding energy arising from the polarizability has been estimated in a previous paper (reference 2) and found to be sufficiently small that for the present considerations we may neglect it.

In Figs. 2 and 3 the energies corresponding to the various representations are plotted against the length of the cube edge. Fig. 2 shows energies arising from the 14 uncrossed bond-eigenfunctions; Fig. 3 shows those from the 28 eigenfunctions. This separation of levels is convenient, but is artificial since all the energies given correspond to doublet states. One observes that all the calculated energies lie considerably higher than the energy for $4\frac{1}{2}$ diatomic molecules (79.7 Cals.) which constitute the initial state for crystallization of gaseous sodium. Hence, as might be expected, the isolated unit cell is still a metastable state. The probability of continued growth only becomes large when the potential energy

[8] N. Rosen, Phys. Rev. **38**, 255 (1931).

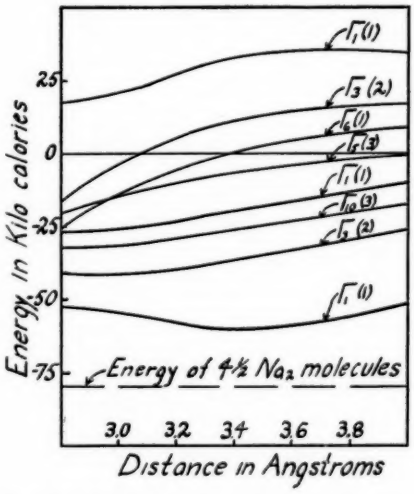

FIG. 2. The number in parenthesis following each Γ_i indicates the degree of degeneracy of the corresponding energy curve. There are thus fourteen energy curves plotted.

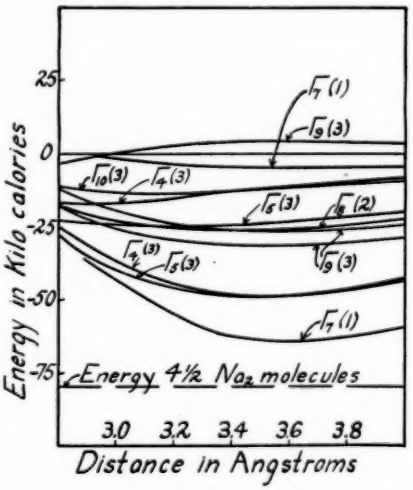

FIG. 3. In this figure are plotted the additional 28 doublet levels of the unit cell of sodium. The energy Γ_7 is lower than Γ_1.

of a crystal nucleus is appreciably lower than that of the molecule from which it was formed. Nuclei containing more than one unit cell will be required to permit rapid crystal growth. The improbability of collisions of such high order is of course the accepted reason for supercooling in the absence of foreign particles.

In the same connection it is interesting to note that comparison of our results with those recorded in an earlier paper (reference 2) indicates that the binding energy of nine sodium atoms on a body-centered cube is less than the binding energy of eight sodium atoms at the corners of the cube with the ninth atom free. The body-centered cube, insofar as we may trust such approximate calculations, is the more stable structure only when it forms a part of considerably larger aggregates, as one might expect.

One of the representations for Γ_7 has associated with it a lower energy than has the completely symmetric state Γ_1 with which the lowest energy is generally associated. Thus it is not always possible, as has sometimes been supposed, to use symmetry alone to single out the eigenfunction yielding the lowest energy.

Of course, the Morse curve does not yield very reliable values for the binding energy for atoms nearer each other than the equilibrium distance (3.15A) by more than a few tenths of an A unit. Also in this region the ratio of coulombic to total energy does not remain constant (0.283) as has been assumed in the calculations, but becomes progressively smaller. However, the energies given in Figs. 2 and 3, although plotted against the distance along the cube edge as abscissa, actually involve energies taken from the Morse curve for this distance and three others (corresponding to α, β, γ and δ). The two distances corresponding to β and γ are of course larger than that corresponding to α. The net result is that the curves are somewhat too low for values of the abscissa much less than 3.0A.

From the figures we also see that because of the interaction of the nine electrons we have 42 doublet levels, fairly near each other in energy, arising from the original lowest level for the nine atoms. This illustrates the type of broadening of spectral lines for this type of collision and shows how the splitting in complicated configurations causes the specific heat to approach more closely the classical value.

THE VECTOR METHOD

We are indebted to Professor Van Vleck for pointing out to us the advantage of the vector method in checking direct calculations of matrix components. This method has been described by Van Vleck,[9] by Seitz and Sherman,[10] and by

[9] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* 76, Oxford Press, 1932. Also Phys. Rev. **45**, 405 (1934).

[10] F. Seitz and A. Sherman, reference 3.

Serber,[11] so that we need give only a very brief indication of its applicability. Dirac showed that a relationship of the type

$$E=Q-\tfrac{1}{2}\sum_{i<j}J_{ij}-2\sum_{i<j}J_{ij}\mathbf{s}_i\cdot\mathbf{s}_j \qquad (9)$$

holds for the matrix components, where J_{ij} is the interchange integral between two electrons in orbitals i and j, respectively, and $\mathbf{s}_i$ and $\mathbf{s}_j$ are the corresponding vectors for electronic angular momentum in units of $h/2\pi$. In the case where eight electrons are in a ^1S state,

$$-2\sum_{i<j}\mathbf{s}_i\cdot\mathbf{s}_j=-\sum_{i=1}^{8}\mathbf{s}_i\cdot\sum_{i=1}^{8}\mathbf{s}_i+\sum_{i=1}^{8}\mathbf{s}_i^2.$$

Now since $\sum_{i=1}^{8}\mathbf{s}_i=0$ and since the product of $\mathbf{s}_i\cdot\mathbf{s}_i$ is $\frac{1}{2}(\frac{1}{2}+1)=\frac{3}{4}$, if all interchange integrals J_{ij} are assumed to have the same value J, Eq. (9) becomes $E_8=Q_8-\frac{1}{2}(8\cdot 7/2)J+8\cdot\frac{3}{4}J=Q_8-8J$. As Van Vleck points out, this ratio of the coefficients of Q_8 and J will hold for non-diagonal as well as for diagonal matrix components for any problem involving eight electrons in a singlet state. It is therefore a very useful check.

This relationship also enables one to see that if orthogonal eigenfunctions are used, the algebraic sum of the coefficients of all interchange integrals for non-diagonal terms is zero. As an example, see the matrix components for the general problem of eight electrons given by Eyring and Kimball.[12] It also enables one to point out that the coefficient of C_8 for $H_{14,14}$ in that paper should be 5/2 instead of 5/4.*

Using the same relationships for nine electrons in a doublet state, for the approximation that all interchange integrals are taken as equal to J, we obtain the equation $E_9=Q_9-\frac{1}{2}(9\cdot 8/2)J+J(-\frac{3}{4}+9\cdot\frac{3}{4})=Q_9-12J$. Hence we have the ratio of the algebraic sum of the coefficients of the interchange integrals to Q_9 in the cases in which we are now interested. This affords another useful check on the matrix components.

Finally we observe that the addition of a ninth electron to the center of a cube will not modify the interaction of the eight corner atoms, i.e., will leave the resultant spin S_8 of the original eight electrons a good quantum number, so that we can write by the methods just described:

$$E_9=E_8+(Q_9-Q_8)-4\delta \\ -\delta[S_9(S_9+1)-\tfrac{3}{4}-S_8(S_8+1)]. \qquad (10)$$

Here the subscripts indicate the number of electrons for which the energy, the coulombic binding, and the spins are, respectively, the resultants. δ is of course the interchange integral for two electrons, one on a corner orbital and the other on the central orbital. There will be two values for the spins, corresponding to the cases of 14 and 28 uncrossed eigenfunctions. S_8 will have the values 0 and 1, respectively, while for all eigenfunctions $S_9=\frac{1}{2}$. E_9 and E_8 are the energies for any root in question, while (Q_9-Q_8) is of course the difference in coulombic binding for the nine and eight electrons and is the same for all 42 roots. We thus see that if we know the energies for the 14 singlet and the 28 triplet states for eight electrons, the vector method enables us to write down at once the energies for the 42 doublet states for nine electrons. For the 14 roots, Eq. (10) leads to the result $E_9=E_8+(Q_9-Q_8)-4\delta$, while for the 28 roots we have $E_9=E_8+(Q_9-Q_8)-2\delta$. The ratio of the coefficient of δ to that of Q is a further valuable check. The fact that the positive potential due to the inner electron with the eight corner ones is only -2δ for Γ_7 and is -4δ for Γ_1 is the reason for the former having the lower root. A more detailed discussion of the connection between the bond and vector methods will be given elsewhere.

[11] R. Serber, Phys. Rev. **45**, 461 (1934).

[12] H. Eyring and G. E. Kimball, J. Chem. Phys. **1**, 239 (1933).

* This was an error in transcription, as has been pointed out elsewhere, and affected none of the applications that were made of this matrix.

The Free Energy of Sulfur Monoxide and the Dissociation Constants of S_2[1]

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Values of $(F^0-E_0^0)/T$ are calculated from spectroscopic data for S_2, SO and S, and equilibrium constants obtained for the reactions

$$2SO=S_2+O_2; \qquad 2SO=\tfrac{1}{2}S_2+SO_2; \qquad S_2=2S.$$

It is found that SO is stable with respect to the first mode of decomposition, but unstable with respect to the second except at higher temperatures.

VICTOR HENRI[4] originally postulated SO to explain a band system lying between 2500A and 3900A observed by him in the emission spectrum from a discharge tube containing sulfur dioxide. Recently, Schenk and others[5] have succeeded in isolating pure SO from the product formed in a condensed electric discharge through sulfur dioxide or a mixture of sulfur vapor and sulfur dioxide at low pressures. They find that at 100°C or at pressures exceeding 50 mm a rapid decomposition sets in according to the equation

$$2SO\rightarrow\tfrac{1}{2}S_2+SO_2,$$

but that at room temperature and lower pressures the gas is quite stable and may be kept for some days in dry vessels. At room temperature there is no reaction with oxygen. The existence of SO as an intermediate compound is indicated spectroscopically for a number of reactions.

In view of the stability of SO it has seemed worth while to calculate from spectroscopic data the free energy change and equilibrium constants for the formation from gaseous S_2 and O_2,

$$\tfrac{1}{2}S_2+\tfrac{1}{2}O_2\rightarrow SO.$$

The F^0/T values for S_2 have also been used to calculate equilibrium constants for

$$S_2\rightarrow 2S.$$

The mathematical methods employed are those given by Kassel.[6] Values of $(F^0-E_0^0)/T$ for O_2 have already been calculated by Johnston and Walker.[7] No correction has been made for the low-lying $^1\Delta$ state,[8,9] the effect of which is certainly negligible at all but the highest one or two temperatures calculated. From the recent analyses of Martin[10] and Naudé and Christy[11] the necessary spectroscopic constants for both SO and S_2 are accurately known. Making minor algebraic rearrangements we may write from Martin's work for the energy levels of SO

$$\epsilon=0.70613(1-0.00796171v)j(j+1)-(1.12884\times10^{-6}-3.20\times10^{-10}v)(j+\tfrac{1}{2})^4+1117.61v-6.116v^2$$

and, from the results of Naudé and Christy for S_2

$$\epsilon=0.40865(1-0.00171296v)j(j+1)-5.2\times10^{-7}(j+\tfrac{1}{2})^4+724.5v-2.91v^2.$$

Both molecules have $^3\Sigma$ normal states. A small unavoidable error is introduced through ignorance of the triplet separations and failure to treat the component levels separately. In the case of S_2 account must be taken of the missing alternate rotational levels. Dissociation from the lower states of SO and S_2 gives normal atoms, the energies of dissociation being for SO, $D''=5.053v$, and for S_2, $D''=4.45v$. These values, together with D'' for O_2[7] give $\Delta E_0^0=-6561$ cal. The atomic energy levels used in the

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate physical chemist (C. W. A.) Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

[3] Associate physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

[4] Henri and Wolff, J. Phys. et Rad. **10**, 81 (1929).

[5] (a) Schenk, Zeits. f. anorg. Chemie **211**, 150 (1933). (b) Cordes and Schenk, Trans. Farad. Soc. **30**, 31 (1934).

[6] Kassel, J. Chem. Phys. **1**, 576 (1933).

[7] Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

[8] Mulliken, Phys. Rev. **32**, 186 (1928).

[9] Lewis and von Elbe, Phys. Rev. **41**, 678 (1932).

[10] Martin, Phys. Rev. **41**, 167 (1932).

[11] (a) Naudé and Christy, Phys. Rev. **37**, 490 (1931). (b) Christy and Naudé, Phys. Rev. **37**, 903 (1931).

calculation of $(F^0-E_0^0)/T$ for S are taken from Bacher and Goudsmit.[12] The lowest lying levels belong to an inverted ^3P state with separations of 398 and 174 cm^{-1}. These are the only levels sufficiently low to have any appreciable effect, the next lowest level, a $^5S_2^0$, being more than 52,000 cm^{-1} higher.

The results of the calculations from spectroscopic data are shown in Table I. The anharmonic

TABLE I. *Free energies and equilibrium constants for SO, O_2, S_2 and S.*

T(°K)	$-\left(\frac{F^0-E_0^0}{T}\right)_{S_2}$	$-\left(\frac{F^0-E_0^0}{T}\right)_{SO}$	$-\left(\frac{F^0-E_0^0}{T}\right)_{S}$	$\log_{10}K=\frac{(SO)}{(S_2)^{\frac{1}{2}}(O_2)^{\frac{1}{2}}}$	$\log_{10}K=\frac{(S)^2}{(S_2)}$
250	45.435	44.838	33.824		−84.896
298.1	46.690	46.068	34.757	5.179	−70.280
300	46.736	46.112	34.791	5.148	−69.799
350	47.850	47.196	35.618	4.463	−58.996
400	48.829	48.141	36.338	3.949	−50.882
450	49.703	48.982	36.976	3.549	−44.562
500	50.495	49.740	37.547	3.228	−39.499
550	51.219	50.433	38.064	2.966	−35.352
600	51.887	51.070	38.535	2.748	−31.892
700	53.085	52.215	39.369	2.405	−26.447
800	54.138	53.221	40.089	2.147	−22.356
900	55.079	54.121	40.721	1.947	−19.169
1000	55.929	54.937	41.284	1.787	−16.615
1250	57.757	56.694	42.470	1.500	−12.008
1500	59.273	58.160	43.431	1.308	− 8.928
1750	60.571	59.418	44.239	1.172	− 6.722
2000	61.705	60.522	44.934	1.069	− 5.063
2500	63.620	62.393	46.089	0.926	− 2.733
3000	65.200	63.943	47.027	0.831	− 1.172
4000	67.722	66.427	48.498	0.711	+ 0.789
5000	69.701	68.382	49.632	0.639	+ 1.974

corrections for SO and S_2 were calculated directly for 250, 298.1, 500, 1000, 2000, 3000, 4000 and 5000°K and carefully interpolated for the other values. The values of column 4 were calculated directly for all the temperatures except 350, 450 and 550°K.

In Table II are given a few values for the equilibrium pressure of SO in contact with liquid or solid sulfur and O_2 (1 atm.). These values are calculated from Table I, vapor pressures of sulfur given by Gruener,[13] and equilibrium constants for the reaction

$$S_8(g)\rightarrow 4S_2(g)$$

extrapolated from the results of Preuner and Schupp.[14] As the thermal data are uncertain, these figures must be interpreted as giving only the order of magnitude of the SO pressure. The accuracy is sufficient, however, to demonstrate the stability of SO with respect to S_2 and O_2.

[12] Bacher and Goudsmit, *Atomic Energy States*, p. 397. McGraw-Hill Co. (1932).

[13] Gruener, Zeits. f. anorg. Chemie **56**, 149 (1908).

[14] Preuner and Schupp, Zeits. f. physik. Chemie **68**, 129 (1909).

TABLE II. *Equilibrium pressures of SO.*

T(°K)	Form of sulfur present	Equilibrium pressure of SO (mm) 1 atm. O_2	1 atm. SO_2
298.1	rhombic	17.8	2.94×10^{-25}
350	rhombic	123	1.59×10^{-20}
400	monoclinic	540	4.10×10^{-17}
450	liquid	1560	1.79×10^{-14}
700	1 atm. S_2	—	1.54×10^{-6}
1000	1 atm. S_2	—	4.05×10^{-3}
1500	1 atm. S_2	—	1.82
2000	1 atm. S_2	—	37.8

ΔF^0 for the reaction

$$\tfrac{1}{2}S_2+SO_2\rightarrow 2SO$$

is directly calculable from Table I and the revised free energy equation for SO_2 given by Eastman.[15] Table II gives also the pressure of SO in equilibrium with SO_2 (1 atm.) at several temperatures above and below the boiling point of sulfur. The values at the four highest temperatures are calculated for S_2 (1 atm.), the others for solid or liquid sulfur. The results indicate that SO is moderately stable with respect to S_2 and SO_2 at flame temperatures, but very unstable below 1000°K.

The dissociation constants for S_2 are given in Table I. These results show that the inconsistent experimental data of Nernst[16] are subject to large errors. This same conclusion is supported by other experimental investigations.[17]

The heat of dissociation of SO_2 to SO and S(g) is about 135,000 cal. and hence the reactions

$$2SO\rightarrow SO_2+S \qquad SO+O_2\rightarrow SO_2+O$$

are 15–20,000 cal. exothermic. It is quite likely, however, that both reactions have activation energies of the order of 50,000 cal. The decomposition of SO is therefore probably a chain reaction, with a lower pressure limit of some 50 mm, and it may be predicted that the oxidation will also be a chain reaction. We may conclude that SO is a respectable substance; it is no more a free radical than O_2, and it is only slightly more susceptible to chain decomposition than are ozone and acetylene.

[15] Eastman, Bureau of Mines Information Circular 6454 (1931).

[16] Nernst, Zeits. f. Elektrochemie **9**, 622 (1903).

[17] See for example, V. Meyer and Biltz, Zeits. f. physik. Chemie **4**, 266 (1889).

The Crystal Structure and Magnetic Susceptibility of Caesium Argentous Auric Chloride, $Cs_2AgAuCl_6$, and Caesium Aurous Auric Chloride, $Cs_2AuAuCl_6$

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The triple salts $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$ have been investigated by means of magnetic susceptibility measurements and x-ray powder photographs in order to obtain information regarding the general nature of these compounds. Both compounds were found to be diamagnetic. X-ray powder-photographic data lead to a cubic structural unit with $a_0=5.33$A for both crystals. The observed intensity values are in general agreement with the perovskite structure. Small discrepancies, however, suggest that the atomic arrangement varies slightly from the ideal perovskite structure. The detailed nature of the distortion was not determined. The bearing of these results on the valence type of the substances is discussed.

IN 1922 Wells[1] discovered an interesting series of triple salts when he attempted to prepare a caesium silver auric chloride, $Cs_6Ag_2Au_3Cl_{17}$, analogous to Pollard's[2] ammonium silver auric chloride, $(NH_4)_6Ag_2Au_3Cl_{17}$. The substance he obtained was a jet black, finely-divided powder with the stoichiometric formula $Cs_2AgAuCl_6$ and properties quite unlike those of Pollard's salt. Further investigation led to the discovery of several other triple salts having the formulae $Cs_2AuAuCl_6$, $Cs_4CuAu_2Cl_{12}$ and $Cs_4HgAu_2Cl_{12}$. All of these compounds crystallize isomorphously, as shown by solid solution formation, and have colors varying from black to light yellow.

In order to obtain information regarding the valence of the metals and the general nature of these compounds, I have investigated two of them, $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$, at the suggestion of Professor Linus Pauling, by means of x-ray powder photographs and magnetic susceptibility measurements. The results of the study are contained in this paper.

We can formulate four reasonable structure types for these salts; (1) Each heavy metal atom may be bivalent and not attached by covalent bonds to other heavy metal atoms. (2) Both heavy metal atoms may be bivalent, the two being joined by a covalent bond forming the group Ag : Au in the case of $Cs_2AgAuCl_6$ and Au : Au in the case of $Cs_2AuAuCl_6$. (3) One heavy metal atom may be univalent and the other trivalent. (4) Each heavy metal atom may resonate between a univalent and a trivalent state.

If the first suggested structure were correct, the compounds would contain groups with an odd number of electrons and hence be paramagnetic. A measurement of their specific magnetic susceptibilities was therefore made by the Gouy method. Both compounds proved to be diamagnetic. The value $\chi=-0.33\times10^{-6}$ c.g.s.m. was found for $Cs_2AgAuCl_6$ and $\chi=-0.25\times10^{-6}$ c.g.s.m. for $Cs_2AuAuCl_6$. The results eliminate a structure with each heavy metal atom bivalent and separate, and we must consider the three remaining structure types.

X-ray powder photographs of $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$ were prepared by using molybdenum radiation filtered through zirconia. These were not entirely satisfactory, the lines being rather faint and difficult to measure. However, it was possible to measure about fifteen lines on each photograph. The regular spacing of the lines suggested at once that the crystals are cubic, and, on assigning indices, all the lines could be accounted for on the basis of cubic units with $a_0=5.33\pm0.02$A for both $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$. The lines which occur, together with their estimated intensities, are shown in Figs. 1 and 2. No lines occurred requiring a larger unit.

These cubic units contain only one-half of a stoichiometric molecule, $Cs_2AgAuCl_6$ or $Cs_2AuAuCl_6$, as estimated from the atomic volumes of the constituent atoms. The calculated values of the density are 4.266 g/cm³ and 4.753 g/cm³, respectively, for $Cs_2AgAuCl_6$ and $Cs_2AuAuCl_6$.

[1] Wells, Am. J. Sci. **3**, 315 (1922).
[2] Pollard, Am. J. Sci. **3**, 257 (1922).

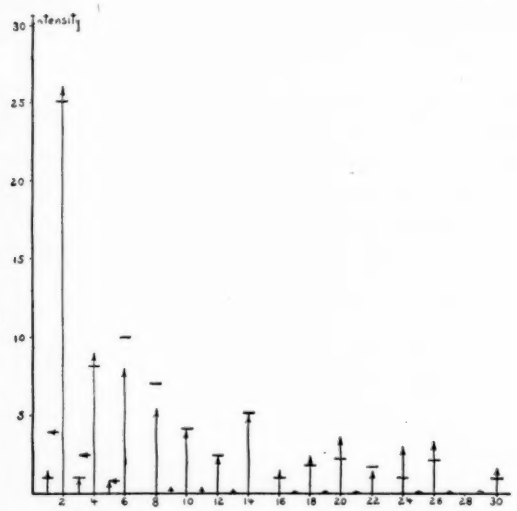

FIG. 1. Powder-photographic x-ray data for $Cs_2AgAuCl_6$. Relative intensities calculated for arrangement *A* are shown by vertical arrows. Horizontal arrows indicate the relative intensities calculated for arrangement *B*. Arrangements *A* and *B* give the same intensities for those lines for which $h^2+k^2+l^2$ is even. Horizontal bars show the observed intensity values.

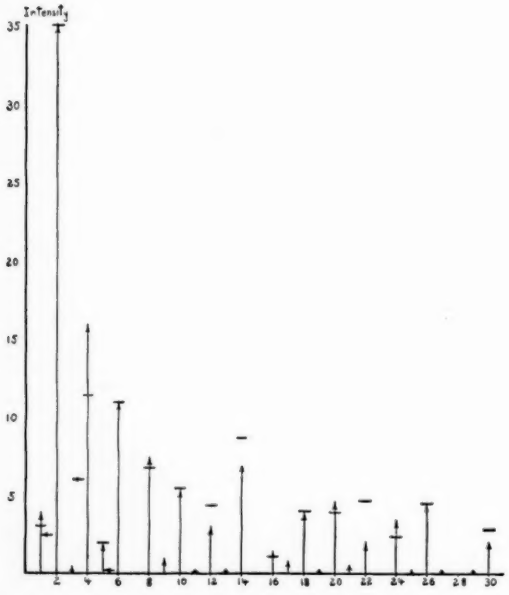

FIG. 2. Powder-photographic x-ray data for $Cs_2AuAuCl_6$. The symbols are the same as for Fig. 1.

No directly measured density values are available for comparison. If these are the true units of structure, the silver compound must contain Ag and Au atoms distributed at random in equivalent positions. We shall first proceed on the assumption that units with $a_0=5.33$A are the true units of structure.

The theory of space groups provides only two ways of arranging 1 M (M=Ag, Au), 1 Cs, and 3 Cl in a cubic unit of structure. These are the following arrangements *A* and *B*.

Arrangement *A*:	Arrangement *B*:
Cs at 000	M at 000
M at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Cs at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
Cl at $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$	Cl at $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$.

The only difference in these forms is the exchange in position of Cs and M.

With the *f*-values of Pauling and Sherman,[3] values of the intensity of reflection from various planes for these two arrangements were calculated according to the usual intensity formula, including the Lorentz, polarization, and frequency factors. Visual estimates of the intensities were made and compared with the theoretical intensities. The results are shown in Figs. 1 and 2. The positions of the vertical arrowheads give the relative calculated intensities for arrangement *A*, and those of the horizontal arrowheads show the values for arrangement *B*. For $h^2+k^2+l^2$ even, both arrangements have the same values. Horizontal bars indicate observed intensities. It is seen that arrangement *B* is in pronounced disagreement with experiment even for simple planes. Thus (111), $h^2+k^2+l^2=3$, for $Cs_2AuAuCl_6$ is not observed, though calculated for arrangement *B* to be over ten times as strong as (210), $h^2+k^2+l^2=5$. Hence the atomic arrangement is *A*. This is known as the perovskite structure. It may be described as a cubic close-packed arrangement of the large atoms Cs and 3 Cl with the smaller metal atoms, *M*, introduced at the centers of octahedra with six chlorine atoms for corners, each chlorine atom forming a corner of two such octahedra.

The agreement in the observed and calculated intensities is sufficiently good to show that this arrangement must be the actual structure of these crystals or very close to it. Therefore, structure type 2 containing Ag : Au and Au : Au complexes is not correct.

If the perovskite structure were the actual structure of these compounds, equivalence of all the gold atoms would be required in $Cs_2AuAuCl_6$;

[3] Pauling and Sherman, Zeits. f. Krist. **81**, 1 (1932).

that is, structure type 4, involving resonance of each metal atom between the univalent and trivalent state, would be correct. However, there are some small discrepancies. The calculated and observed intensities of the lines $h^2+k^2+l^2=24$ in Fig. 1 and $h^2+k^2+l^2=22$ in Fig. 2 show definite disagreement when compared with the values of neighboring lines. These discrepancies are sufficient to eliminate the perovskite structure and the valence type 4. It is probable that the structures are based on a larger unit and that the atomic arrangement is a distortion of the perovskite structure so that the six chlorine atoms are brought closer to the trivalent gold atom (valence type 3) than to the univalent gold or silver atom. The data are not sufficiently extensive to permit the detailed discussion of this point. We hope to continue the investigation and to determine completely the structure of these crystals.

The Line Absorption Spectrum of Crystalline $KCr(SO_4)_2 \cdot 12H_2O$

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(Received March 24, 1934)

The line absorption spectrum of chrome alum has been photographed at five temperatures from 85° to 14°K. The variation with temperature of the intensities of certain of these lines suggests the existence of one or more excited lower levels. At 14°K a new group of faint, sharp lines appears near 4500A. A general discussion of the nature of energy levels in solids is presented and the possible energy states which could give rise to the observed lines are examined theoretically.

IT is commonly known that the outermost electrons in the atoms of a substance determine most of its chemical and many of its physical properties. Therefore, given a reasonably complete knowledge of those energy states of the substance which involve the outer electrons, one should be able to predict most of its properties. Conversely every property of the substance should give some information concerning its energy levels. Though the work of correlation is as yet far from being fully developed, considerable progress has been made. Thus, for example, the energy states of many monatomic and diatomic gases have been related to such properties as heats of activation and dissociation, entropy, magnetic susceptibility and the like. In the case of polyatomic gases and solids progress has been slower due to the greater complexities of the problem but now that the nature of the difficulties is better understood, more rapid headway is being made.

With gases a study of the spectra both in emission and absorption has provided by far the most direct and fruitful method of determining energy states. Unfortunately, in the case of most solids the emission spectra are not characteristic and the absorption spectra at room temperature consist usually of wide structureless bands showing none of the detail which is so necessary if an analysis is to be made. Nevertheless, if particular compounds are chosen, and especially if they are cooled to very low temperatures, sharp absorption lines can be obtained and the energy levels may be deduced as in the case of gases.

Up to the present most of the work on the spectra of solids has been done with compounds of the rare earth metals, chiefly because they are rich in lines which become sharp at higher temperatures than do the lines of commoner compounds. The reasons for this have been discussed in a previous paper.[2] The chief disadvantage of working with the rare earth compounds is that their properties are not as well known as might be desired, mainly due to the fact that they are not available in any quantity for experimental purposes. Moreover, the spectra

[1] DuPont Fellow in Chemistry 1932–33; Shell Research Fellow in Chemistry 1933–34.

[2] Spedding and Nutting, J. Am. Chem. Soc. **55**, 496 (1933).

of the gaseous rare earth ions are very complicated and have not yet been analyzed. It is desirable therefore to investigate some compounds whose properties are well known, and it is also desirable that in these compounds the metallic elements with which the color is associated shall have had their gaseous spectra interpreted. The compounds of chromium answer these requirements and some fine exploratory work has been done in this field.[3, 4, 5] Unfortunately the men doing this work were able to cool their crystals only to liquid air temperatures. Since the lines at these temperatures are considerably broadened due to thermal agitation it seemed advisable to investigate a chromium compound at liquid hydrogen temperatures under as high dispersion as was available. Chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$, was chosen for these investigations because its properties are well known and because it crystallizes in the isometric system. The chromium ion in the solid alum is subjected to electric fields of high symmetry and its spectroscopic terms may be treated theoretically, perhaps according to the method of Bethe.[6]

Experimental Part

Mallinckrodt's C.P. chrome alum was dissolved in cold water and evaporated at the temperature of the room in order to secure small seed crystals. Some of the best of these were suspended from silver wires in the alum solution, which was allowed to evaporate further at 25°, perfect crystals from 2–5 cm on an edge being obtained in this way. The crystal fragments photographed were usually about 1×2 cm in cross section and varied in thickness from 1.9 to 5.7 mm. The crystal sections were placed directly in the cooling liquids at the center of a Dewar flask of 11 cm inside diameter and being thus surrounded by 5 cm of the liquid air or liquid hydrogen, were presumably very nearly as cold as the baths themselves. Light from a 500 watt tungsten lamp, after being filtered through 10 cm of water, was focussed on the crystal, and the light from this was thrown on the slit of a 3 meter grating in Paschen mount. The grating has 58,000 lines and the dispersion in the first order, which was used exclusively, is 5.3A per mm. The slit width was 0.04 mm. Exposure times varied from 2 to 28 hours, and on this account the temperature of the grating room was kept constant within 0.1°C. Photographs were made on Eastman 50 plates in the violet and on Wratten Hypersensitive Panchromatic plates in the green and red.

The position of members of the group of sharp absorption lines appearing between 6685–6730A and 4450–4550A were measured with reference to the iron arc spectrum directly on a comparator, while the fuzzier lines lying at 6300–6700A were measured from microphotometer curves and enlargements.

Absorption spectra were obtained along two crystallographic directions and at the temperatures of liquid and solid air and of liquid and solid hydrogen, 85° and 60°, 20° and 14°, respectively, and in addition at a temperature which we estimate at about 40°K. This last temperature was attained by a crystal immersed in liquid hydrogen in a Dewar designed for Zeeman effect work. The inner square tube of the narrow extension at the bottom of the flask was only 9 mm on a side so that rising bubbles of gas in forcing their way through the small space between the wall and the crystal very frequently came into contact with the crystal face thereby materially decreasing the rate of heat transfer from the crystal. As before, the light source was a tungsten lamp, but the rays were this time filtered through 10 cm of a saturated solution of potash alum and 30 cm of water, and in addition through Wratten filter No. 70 and Jena filter BG15. Still, enough absorbable radiation reached the crystal to warm it to a temperature which, from the breadths of the absorption lines, we judge to be near 40°. The photograph was made with a Hilger E185 5-prism spectrograph giving dispersion of 5A per mm at 6700A. The 6700A lines alone were photographed. (See Figs. 1 and 2.)

At 85° chrome alum shows continuous absorption throughout the visible and near ultra-

[3] Joos and Schnetzler, Zeits. f. physik. Chemie **B20**, 1 (1933).

[4] Sauer, Ann. d. Physik IV, **87**, 197 (1928).

[5] Snow and Rawlins, Proc. Camb. Phil. Soc. **28**, 522 (1932).

[6] Bethe, Ann. d. Physik **3**, 133 (1929); Zeits. f. Physik **60**, 218 (1930).

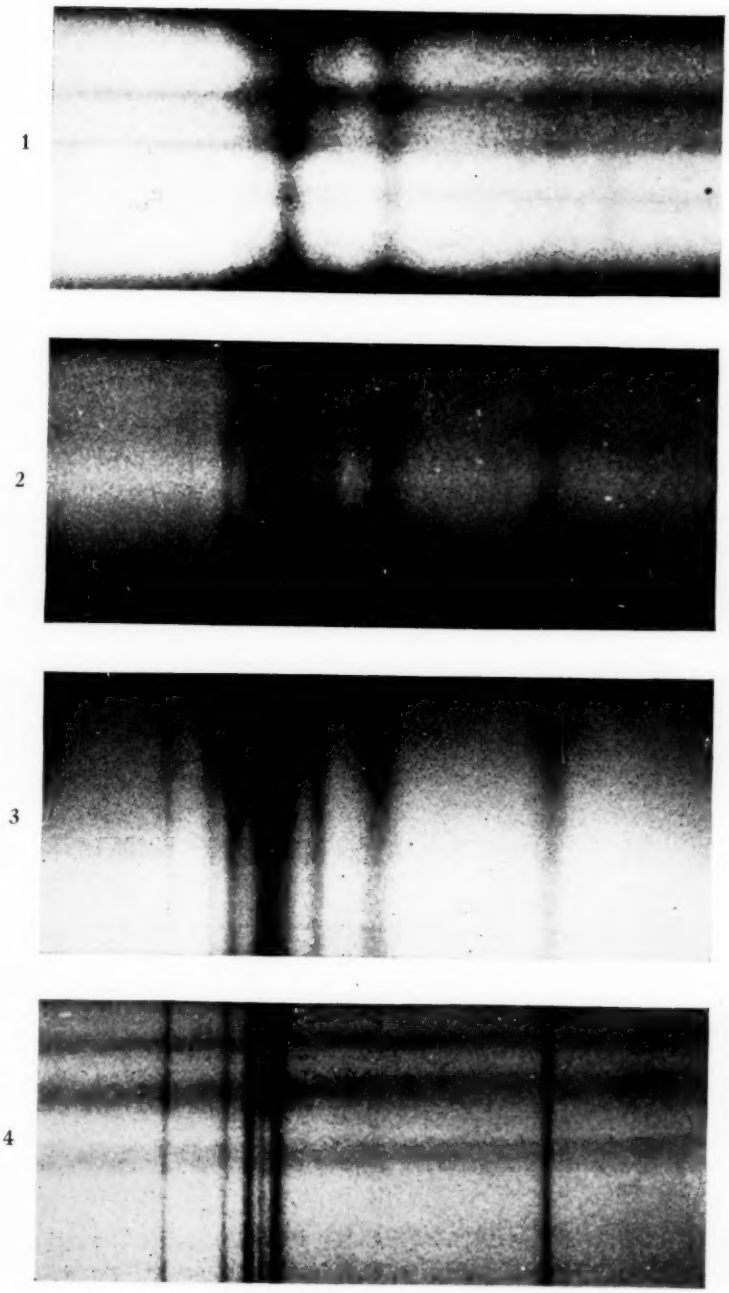

FIG. 1. Enlarged reproductions of the 6700A multiplet in chrome alum. 1. Temperature 85°K; thickness 5.7 mm; light passed ⊥(111) plane. 2. 60°K, 4.5 mm, ⊥(010). 3. 40°K, 3.4 mm, ⊥(111). 4. 14°K, 4.5 mm, ⊥(010).

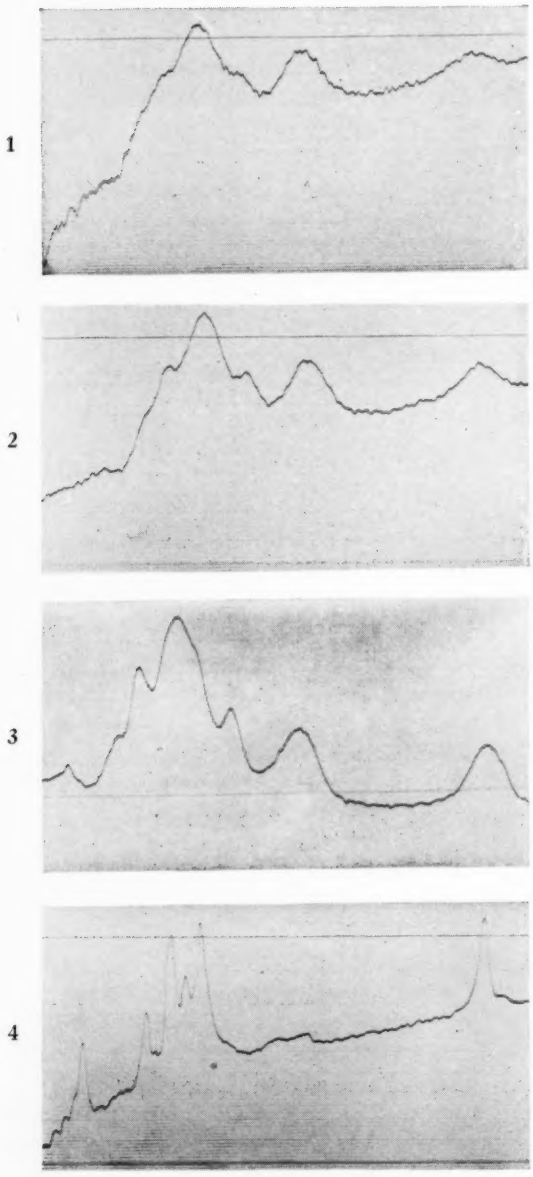

FIG. 2. Microphotometer curves of the 6700A multiplet in chrome alum. 1. Temperature 85°K, thickness 5.7 mm, light passed ⊥(111) plane. 2. 60°K, 4.5 mm, ⊥(010). 3. 40°K, 3.4 mm, ⊥(111). 4. 14°K, 4.5 mm, ⊥(010).

violet except for a region between 6300 and 7000A. Within the transmission band there are a number of weak, indistinct lines and in the neighborhood of 6700A a group of stronger, sharper lines, of which two are so prominent that they are quite appropriately known as the characteristic doublet.

The effects of changing the thickness of the crystal and the direction of the beam of light through the crystal may be given in a few words. Increasing the thickness merely narrows the regions of transmission and intensifies the absorption lines, as would be expected. Varying the relative orientation of the exciting light and the crystal axes brings about changes in the intensity but not in the position of the absorption lines. Considerable intensity differences are not noted at all in the hydrogen pictures or in the doublet and its companions at the temperature of liquid air. However, in the latter case when the incident light enters the crystal perpendicular to an (010) plane the weak, diffuse lines on the short wave-length side of the doublet appear much more prominently than when the beam is perpendicular to a natural (111) face.

The temperature effects are much greater. Differences in the characteristic group are not remarkable between any two successive temperatures, but the appearance of the doublet at 85° and at 14° is strikingly different. The long wave-length component resolves and practically disappears, while the other component becomes five lines, of which two are very strong. In addition, an entirely new line becomes visible on the violet side of the short wave-length component and an originally weak line to the red side of the doublet becomes much more prominent, and appears with a satellite of its own.

At 14° the diffuse lines showing between 6650 and 6450A at 85° are intensified and sharpened somewhat, and a number of new lines appear, but there is no such radical alteration as is noted in the characteristic lines. Sauer's assumption that the width of these weak lines should decrease as the square root of the temperature seems not to be justified at all.

At the lowest temperature a transmission band showing in the continuum at about 4500A demonstrates a structure of dim, narrow absorption lines which to the eye appear equally spaced. Precise measurement does not corroborate this observation however. Sauer looked for some such phenomenon as evidence of the superposition of lattice vibrations on an electronic and perhaps also vibrational jump, and he has announced a group of lines in the chrome selenates in the region 6300–6400A having con-

stant frequency differences equal to 43 cm^{-1} in the KCr− and 44 cm^{-1} in the RbCr− alum. On our own plates the corresponding lines in the potassium chrome sulfate at 20° and 14° appear to be distributed almost at random.

Sauer has found that the absorption spectra of caesium-chrome and methylamine-chrome alums correspond with one another but not with the spectra of the other alums, and he very plausibly explains this as due to an alteration of the crystal lattice, which however is not reflected in a change in the external symmetry of the crystal. He has also noted that even potassium chrome alum is to some extent anomalous in that the separation of the doublet components is 11A, while for most of the other alums the figure varies from two to four. The fading of the red component and the development in the violet component of two strong lines of 3.1A separation suggests that at some temperature below that of liquid air a crystal transformation takes place which removes the abnormality of the potassium alum.

We reject this explanation because the change is evidently a rapid, reversible one, which takes place not at one definite temperature but more or less continuously over the whole range from 85° to 14°. A sudden alteration in the symmetry of the crystal lattice would doubtless be attended by the sudden fading of some of the absorption lines, while new lines might make their appearance. It is questionable that in a solid like chrome alum a change in the lattice structure could take place at temperatures of 85°K and below except during a very long period of time, but if it did, it would be expected to take place within a well-marked and rather small temperature range. On the other hand a gradual alteration of the lattice with decreasing temperature should bring about a progressive, continuous shift in the lines from the positions they occupy at the highest temperature to the positions they occupy at the lowest temperature. Rather than this we have found that lowering the temperature of the crystal changes the intensity of certain of the absorption lines enormously, but leaves their wave-lengths approximately the same.

We believe that most of the alterations in the spectrum as the temperature is raised are caused by a very rapidly increasing congregation in two or more excited states of ions which had been previously in the basic state. If this were to occur it would be evidenced by the appearance of new lines shifted to the red side of the original low temperature ones (all of which must have come from transitions from the common ground level) by the amount of the separation of the basic and excited lower levels. There would not necessarily be a complete new set of lines, for selection rules might well forbid a transition between an excited lower level and a given upper level, while the transition from the basic level to the same upper level would be permitted. If we disregard the statistical weights, which will probably not differ by a factor of more than two or three, and if A_0 is the number of ions in the ground state, then the number A_1 in an excited state is equal to $A_0 e^{-h\nu/kT}$, where ν is the separation of the two states. If ν is of the order of 100 cm^{-1}, A_1 even at 85°, the highest temperature at which we worked, will be small and absorption lines originating at the upper level will be extremely weak. On the other hand, if ν is only 10 cm^{-1}, A_0 and A_1 will not be very different at 14° and will not change much in the temperature range 14°–85°. For a group of intermediate values of ν, A_1 must change very rapidly within this temperature interval, while A_0 is always a large faction of its original value. With a rapidly increasing value of A_1, a rapid enhancement of the new lines is to be looked for, while the original lines should still be strong. Simple calculation shows that in the temperature range 20–60° (in which we have noted a very marked increase in intensity of three of the absorption lines) there is a particularly rapid increase in the population of a level of the lower multiplet situated about 40 cm^{-1} above the basic level.

We have distinguished three high temperature lines, which appear at 85° at λ6708.7, 6702.6, and 6690.9A. The λ6690.9 line is weak at best and no trace of it is found below 40°K, but, with the fading of the λ6708.7 and 6702.6 lines, two other lines situated about 38 cm^{-1} to the violet become markedly stronger. If λ6692 and λ6708 are indeed related in having a common excited level, it might be expected that they would present a similar appearance, whereas it is evident from the photographs and the micro-

TABLE I.

λ	ν	Int.	Type	λ	ν	Int.	Type
14° and 20°K							
6730.03±0.1	14854.7	1	L	6456.4 ±0.2	15484.2		
6728.12±0.1	14858.9	10	L	6451.8 ±0.5 M	15495.3		
6708.6 ±1	14902	1	H	6440.0 ±1	15524		
6705.7 ±1	14909	1	H(L?)	6420.9 ±1 M	15570		
6701.4 ±1	14918	1	H	6365.4 ±1	15706		
6697.83±0.1	14926.1	10	L	6347.9 ±1 M	15749		
6696.26±0.1	14929.6	4	L(H?)	6310.0 ±1 M	15844		
6694.73±0.1	14933.0	10	L	6298.8 ±1 M	15872		
6693.26±0.2	14936.3	1	L				
6692.06±0.1	14939.0	4	L	4554.9 ±1	21948		
6685.32±0.2	14954.0	4	L	4549.0 ±1	21977		
				4537.8 ±1	22031		
6673.1 ±1	14981			4531.6 ±1	22061		
6662.4 ±1	15006			4526.8 ±1	22085		
6642.7 ±1 M	15050			4520.3 ±1	22116		
6625.0 ±1	15090			4513.9 ±1	22148		
6612.2 ±1 T	15119			4506.3 ±1	22185		
6588.9 ±1	15173			4500.2 ±1	22215		
6550.5 ±0.5	15261.8			4476.3 ±1	22334		
6491.6 ±0.5	15400.3			4468.0 ±1	22375		
6481.7 ±0.5	15423.8			4461.0 ±1	22410		
6467.2 ±1 M	15458			4453.0 ±1	22451		
6462 ±1	15471						
40°K				60° and 85°K			
6728.0 ±0.5	14859.1	6	L	6727.03±0.5	14861.3	4	L
6708.7 ±0.5	14901.9	6	H	6708.73±0.5	14901.8	6	H
6701.9 ±0.5	14917.1	5	H	6702.57±0.5	14915.5	3	H
6698.5 ±0.5	14924.7	5	L	6697.68±0.5	14926.4	10	L
6696.8 ±0.5	14928.4	10	L(H?)	6693.57±0.5	14935.6	4	L
6695.4 ±0.5	14931.6	5	L	6690.9 ±1	14942	1	H
6692.3 ±0.5	14938.4	5	L	6642.5 ±1 M	15050		
6689.8 ±0.5	14944.0	2	H	6625 ±2	15090		
6685.3 ±0.5	14954.0	1	L	6612 ±2 M	15120		
				6590 ±2	15171		
				6552 ±2 M	15259		
				6504 ±2	15372		
				6491 ±2	15402		
				6481 ±2	15425		
				6467.3 ±1	15458		
				6462 ±2	15472		
				6454 ±2 M	15491		

T indicates a triple line; M a line which is multiple and unresolved.

photometer traces that λ6708 is much broader than the other. The cause of the unusual breadth must be looked for in a lower state which is unusually wide for a reason which we can only guess, but which may perhaps be found in a small magnetic interaction among neighboring chromium ions in the lattice.

In Table I are given the positions of the lines observed in chrome alum at the various temperatures. The 6700A lines have been classified as being either high temperature or low temperature lines, and a rough estimate of their intensities has been made. The data given for 20° and 14°K have been taken from measurements of three plates and the data for 85° and 60° from five plates, while those for 40° have come from a single photograph.

DISCUSSION OF RESULTS

In view of the conflicting opinions in the literature as to the origin of the lines and bands that appear in chrome alum, we shall first consider in a rough, qualitative fashion what one might expect to find in the way of energy levels

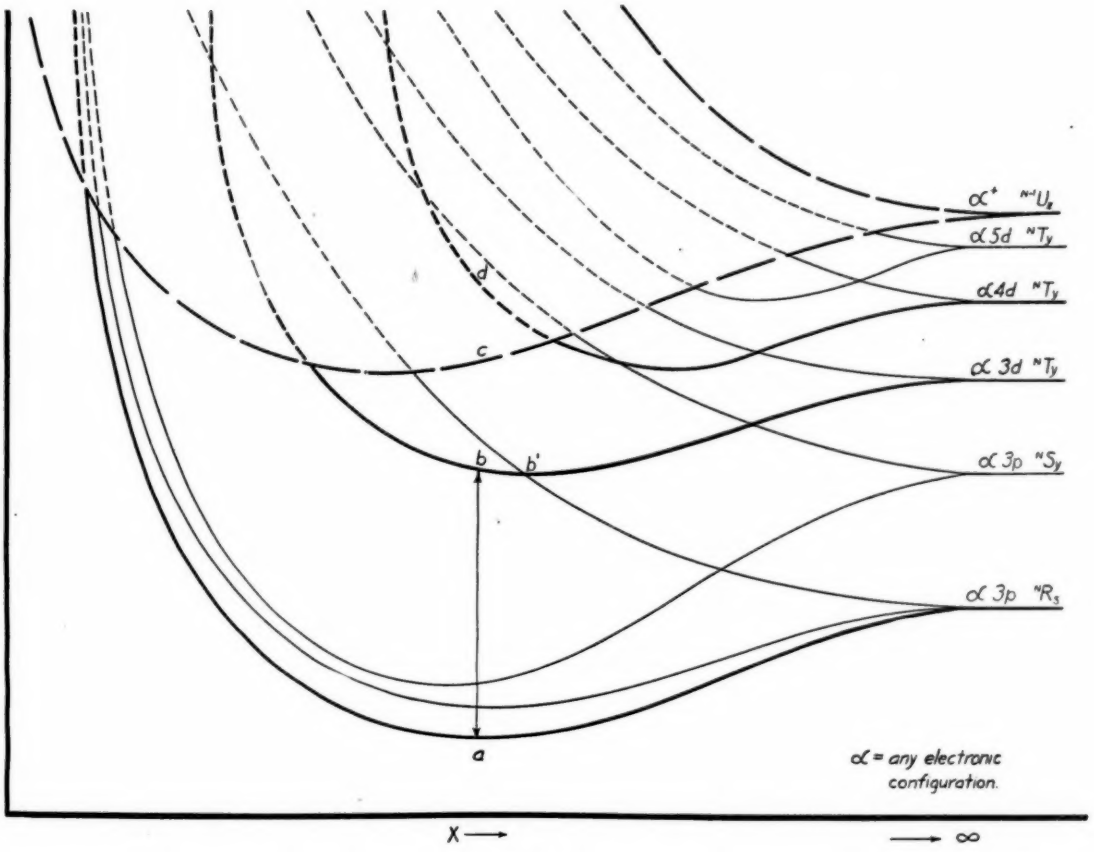

FIG. 3.

in a solid. There are many methods by which this can be done theoretically.[6a] The one we shall use is to consider what will happen to the energy states of a free ion when it is placed at the center of a crystal lattice. While one cannot carry out the following procedure experimentally one can imagine that a crystal has been expanded until the neighboring atoms reach infinity. Then the central atom or ion will be very little influenced by the fields of the neighboring atoms and will have the energy states of the free gaseous atom or ion. In Fig. 3 are plotted the values of the energy levels against x, where x is the size of the unit cell of the crystal. On the right, where x is infinity, are given the energy states of the free ion, with their electronic configurations and spectroscopic terms. Since this diagram can represent any atom, the spectroscopic terms and electronic configurations are expressed in general symbols.

Now if one imagines the crystal lattice to be slowly contracted, since all atoms are made up of positive and negative charges of electricity, the neighboring atoms will begin to exert electric forces on the central atom. It is known from the Stark effect that the orbits of an atom tend to couple with an electric field in different ways so as to give states of slightly different energies. This will cause the original states to split into several components. As the lattice contracts more and more, the fields will become greater and therefore the splitting will become large. Finally a point will be reached where the strength of the fields of the neighboring atoms will be of the same order of magnitude as the inner atomic fields of the central atom. Then a strong Stark effect will appear and molecular type coupling will occur. The levels will resemble the type of

[6a] Bethe has treated this problem in a few simple cases on the basis of quantum mechanics and group theory.

levels deduced from band spectra. If the lattice is compressed still further, strong repulsive forces will come into play and it will take considerable energy to maintain the atoms in these states. The minimum occurring at a will of course represent the formation of a stable compound or crystal lattice.

The excited spectroscopic states arising from electronic configurations where an electron is farther from the nucleus will behave in much the same manner as the crystal lattice is contracted. Here, however, the minima will be shifted to the right since the electron is farther from the center and will therefore be affected by the electric fields earlier. The minimum at b' would represent the formation of a stable lattice if all the atoms could be excited to this state.

Finally in the ionized state, the remaining electrons will also be subjected to the action of the electric fields as the crystal is contracted. However in this case since the electrons are close to the nucleus, the fields will not be effective so soon and the minimum will be shifted to the left.

It should be pointed out that there are really two types of ionization in a solid, the one where the electron is removed completely from the crystal lattice, and the other where the electron is removed from sharp quantitization with the central atom but still remains in the lattice free to move, as exemplified by metallic conduction.

One can see from a diagram such as this what the best conditions would be for observing sharp absorption lines in a solid. Thus if an atom were excited from state a to state b, a sharp absorption line would be observed at low temperatures. It can be seen that the main requirement for the existence of states such as b is that they arise from electronic configurations where the electrons remain close to the nucleus. If the atom is excited to c a broad band will be observed, for while it takes a definite amount of energy to ionize the atom the departing electron can absorb various additional amounts since it is free to take up kinetic energy in the lattice. If, again, we are able to excite atoms to state d, the sharpness of the line observed will depend upon the ease with which the electron may free itself, leaving the atom in state c. If the selection rules completely forbid this change the line will be very sharp. If they permit it to a small degree

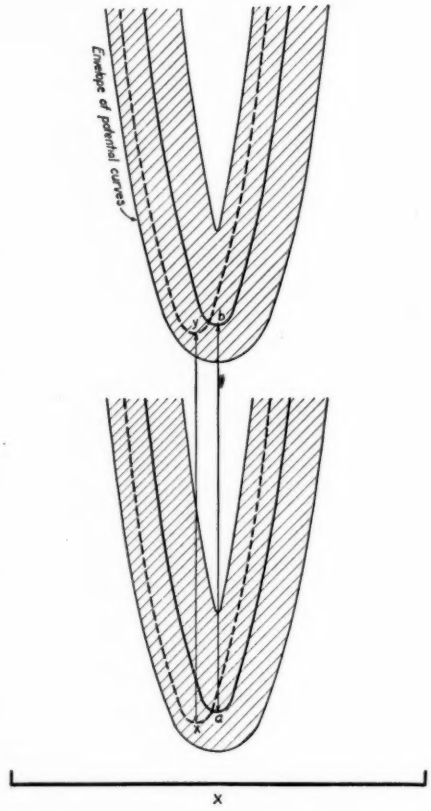

FIG. 4.

the lifetime in d will be shortened and the line will be diffuse, and finally if they permit it freely the lifetime in d will be extremely short and the absorption band observed will appear as part of the band arising from $a \rightarrow c$.

All the bands should become sharper and those produced by transitions such as $a \rightarrow b$ extremely sharp when the temperature is greatly lowered. In Fig. 3 for simplicity in plotting we have permitted only the size of the unit cell to vary. Actually in a solid, while the size of the crystal lattice will not change very greatly as the temperature increases, its shape and symmetry will vary slightly due to the increased agitation of its component atoms. This will cause corresponding shifts in the potential energy curves. The curve for levels of the a and b type, where the unit cell is fixed and the central atom is allowed to vary its position, will appear as in Fig. 4. If the shape of the cell changes slightly the minima will be shifted either to right or left or up and down depending on the nature of the

distortion. Since the absorption is due to transitions within millions of atoms, at higher temperatures the transition in some atoms will be from a to b and in others from x to y and the net result observed will be a blurred band. On the other hand at low temperatures all the atoms will be close to their equilibrium positions so that all transitions will be from a to b and the light absorbed will be approximately monochromatic. The potential curves are of course tremendously steep because the motion of an atom in a crystal is rigorously constrained.

Compounds of the metals of the rare earths and of the first transition group are the most suitable for observing sharp absorption lines, for atoms of the elements of both groups have incomplete shells, whose electrons can couple to give a number of levels of the b type.

It should be emphasized that Figs. 3 and 4 are to be regarded as only roughly indicative of the nature of energy levels in solids. While in these diagrams for simplicity in plotting we have allowed only one variable to change, the difference between these representations and the truer ones in n dimensions is one of complexity and not of principle. Although it has not been indicated on the diagram, at different points along the x coordinate different states may be lowest and two or more stable crystal forms may exist. While under a given set of conditions one form will be the most stable, another may be possible as a metastable state and a considerable amount of energy may be required to carry the atoms over the potential barrier which separates the two states. If one of the ionized states should happen to be lowest some of the electrons will be free in the lattice and the substance will behave as a metal. Since the minima of the ionized (metallic) states usually occur at the left in the potential energy diagram, corresponding to smaller interatomic distances, if a substance exists in two forms the more metallic one will be the denser.

There is still another type of solid which shows sharp lines at low temperatures. This is the type in which the gaseous molecules enter the crystal lattice without undergoing any very marked change. In this molecular type solid, where the molecules are held together by van der Waals forces, the absorption spectrum resembles closely that of the gas. Many organic compounds belong to this classification, particularly the benzene derivatives that have been so excellently investigated by Professor Pringsheim[7] and his coworkers.

Since the spectra of the polyatomic gaseous molecules have not been analyzed, it would be very difficult to interpret the spectra of the solids and we shall not discuss this type in detail in this paper.

To return to the specific case of chrome alum which we are investigating, White[8] has analyzed the gaseous spectrum of Cr IV and finds its lowest term is a $^4F_{3/2}$, which arises from the electronic configuration $1s^22s^22p^63s^23p^63d^3$. He has also located a ^2G and a ^2H term, arising from the same electronic configuration, which lie 15,000 and 21,000 cm^{-1}, respectively, above the basic term. While transitions between these states are forbidden in the case of the gas, Saha,[9] Deutschbein[10] and others have pointed out that in solids they may occur and probably account for the lines and bands appearing in crystals and solutions of chromic salts.

de Haas, Gorter and van den Handel[11] have shown that for chrome alum the reciprocal of the paramagnetic susceptibility is a linear function of the absolute temperature over the range from 290° to 1.34°K, and that the slope of the line is precisely that calculated on the assumption that only the spins of the $3d$ electrons of Cr^{+++} orient in a magnetic field, the orbital moments being suppressed. The electric fields in the crystal must then be strong enough to break down the L–S coupling that occurs in the gas and as has been pointed out elsewhere[12] the J quantum number is meaningless. The fact that the sharp lines appear at 15,000 cm^{-1} as well as at 21,000 cm^{-1} would seem to indicate that the $\Sigma l = L$ coupling has not been broken, for since the ^4F, ^2G and ^2H terms all arise from the same electronic configuration, if the l–l coupling had

[7] Pringsheim, Zeits. f. Physik **40**, 75 (1926); Kronenberger, Zeits. f. Physik **63**, 494 (1930).

[8] White, Phys. Rev. **33**, 672 (1929).

[9] Saha, Nature **125**, 63 (1930).

[10] Deutschbein, Zeits. f. Physik **77**, 489 (1932).

[11] de Haas, Gorter and van den Handel, Proc. Acad. Sci. Amsterdam **33**, 676 (1930); **36**, 158 (1933).

[12] Spedding, Phys. Rev. **43**, 143 (1933).

been broken, the centers of the multiplets would be greatly displaced by the crystal fields.

From three equivalent d electrons ^4P, ^2P, ^2D and ^2F terms also arise, and while White has not located them in Cr IV they must nevertheless exist. Most of them have been found in Ti II and V III and if extrapolations are made to Cr IV, the ^4P term falls close to the ^2G and the ^2D close to the ^2H, while ^2P lies in the near infrared and ^2F in the near ultraviolet. The absorption lines of chromium compounds might come as well from transitions to the ^4P, ^2P, ^2D and ^2F as to the ^2G and ^2H states. These states are so spread over the spectrum that even if the crystal fields were intense enough to break the Σl coupling, multiplets would still occur in the regions of observed absorption. The fact that substituting NH_3 for H_2O about the Cr^{+++} ion is sufficient to shift the lines hundreds of wave numbers[3] might be considered as evidence in favor of this very strong field case.

Measurements on a preliminary photograph of the Zeeman effect in the sharp line group indicate a g factor of approximately 2, as might be anticipated from the magnetic susceptibility data. The terms in the excited multiplets are closer together than one would expect on the basis of linear Stark fields which were sufficient to break down the L–S coupling, but it may be that in fields of cubic symmetry, the splitting which corresponds to the strong field case would not have to be so great. The close splitting occurs not only in the excited terms but in the basic one as well, for we have shown that besides the lowest level, a level is present at about 38 cm^{-1}, and in Sauer's microphotometer curves evidence is seen of another still higher state, present at $+18°$ and $-78°$C, but which has faded out at the temperature of liquid air.

These low levels are interesting in light of the magnetic measurements, since they must give the same susceptibility as the basic level, and the interaction among them, such as Van Vleck[13] found in the nitric oxide levels must be very small. The low levels do not fit into the theory which Van Vleck and Schlapp and Penney[14] have advanced to explain the magnetic susceptibility of salts of the elements of the first transition group. They may perhaps be vibrational frequencies superposed on the lowest electronic term but we think this is unlikely since there is none of the regular spacing of the lines that one usually finds when such vibrations couple with electronic states. Moreover, in the excited states the wide spread of the multiplets which one might expect to find if the close lines were due to vibrations and the electric fields had split the multiplets far apart, is not observed. A further objection to this proposal is that in compounds of gadolinium, whose basic state is known to be single, such vibrational levels are not found. On the other hand, in solids where there is such vibrational coupling, as for example in uranyl salts, nitrates, permanganates and chromates, regular spacing of the bands is noted.

The weak lines which lie between 6300 and 6700A differ distinctly from the characteristic group in their behavior with changing temperature. In fact, except that both groups must have their origin in the same ground state, we can see no kinship between them. We are inclined to attribute the faint lines to transitions to multiplets arising from other spectroscopic terms, possibly to terms coming from such configurations as $3d^24s$ or $3d^24p$, or possibly to transitions of the type $a \rightarrow d$ in Fig. 3, where the upper states are unstable and short-lived since, with the dropping back of the electron, the Cr^{+++} can pass into a state of higher ionization. It is notable that even at 14° these lines are almost as diffuse as they are at the temperature of liquid air.

The origin of the broad continua which occur in several places through the spectrum we think may lie in transitions to ionized states. The

[13] Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, 1932.

[14] Schlapp and Penney (Phys. Rev. **42**, 666 (1932)), to account for the observed magnetic susceptibility have calculated on the basis of their theory that the ^4F term must be split by the crystal fields by about 9 volts. Since the ^4P term which arises from the same configuration lies only about 1.5 volts above the ^4F term there would be strong interaction between them in fields of this magnitude. The problem would therefore have to be treated on the basis of the very strong field case of $3d$ electrons.

positions of these bands are very sensitive to variation in temperature, and their edges draw in several hundred Angstroms between room and liquid hydrogen temperatures. It is the narrowing of two of these bands which makes it possible for the sharp lines at 21,000 cm^{-1} to be observed at the lowest temperatures.

Bose and Datta[15] ascribe both the bands and the sharp lines to the $^4F-^2G$ and $^4F-^2H$ transitions. They believe the former are due to jumps in Cr^{+++} ions whose orbital moment has been quenched by interaction with the water molecules which surround the ion, leaving only the spin free. The lines are supposed to originate in transitions in a far smaller number of ions which have become relatively gas-like. This explanation seems unreasonable, for it is difficult to conceive that in a solid at the temperature of liquid hydrogen there are holes in which chromium ions are so uninfluenced by their neighbors as to be distinctly different from the average chromium ion. Besides, the g factor of 2 deduced from the Zeeman effect of the sharp line group indicates that here also the orbital moment of the ions in the basic state has been quenched. On the other hand the conjecture that the broad bands result from transitions to metal-like states is in satisfactory accordance with their behavior toward changing temperature. It is interesting in this connection that certain colored compounds, for example cuprous oxide, show a marked increase in electrical conductivity when they are illuminated with visible light.[16]

The very low intensity of the sharp absorption lines is, we think, related to the fact that transitions between terms arising from the same electronic configuration are forbidden in gases, and while in crystals the states may be perturbed enough to permit the jumps, the probabilities will nevertheless be small. It may be that it is the magnetic fields of the Cr^{+++} ions acting on each other that make the transitions possible, for the characteristic lines in a mixed crystal of potassium aluminum alum and chrome alum are much less intense than one would expect from the number of chromium ions present.

Low temperature lines which fade out as the temperature is raised we think may originate in transitions to upper states of the d type in which selection rules forbid the ion to drop back into the c state of further ionization. With increasing thermal vibration of the lattice the increasing fluctuation of the electric fields may cause these selection rules to be broken. The temperature at which the fluctuations are sufficient noticeably to invalidate the selection rules may be different for different lines.

[15] Bose and Datta, Zeits. f. Physik **80**, 376 (1933).

[16] Joffé and Joffé, Nature **132**, 168 (1933).

The Degeneracy, Selection Rules, and Other Properties of the Normal Vibrations of Certain Polyatomic Molecules

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The number, degeneracies, and symmetries of the normal modes of vibration are given for molecules in which several atoms are bonded to a central atom. Ninety-nine symmetries, including all possible structures with three to seven atoms and the more important structures of eight and nine atoms are listed in tables. The selection rules for the Raman and infrared spectra are included as well as the polarization properties of the Raman lines and the rotational structure of the vibrational bands. In a number of more important cases figures are given showing the normal modes of vibration. Many examples of molecules which are believed to possess certain of the structures are included in the tables, together with references to experimental papers dealing with them.

IN drawing structural conclusions from observed Raman and infrared spectra, it is necessary to know the number of normal frequencies of vibration and the selection rules which characterize the various possible configurations of atoms. The theory of the number and degeneracy of the normal vibrations of symmetric molecules, first developed by Brester,[1] was very concisely expressed by Wigner,[2] using group theory, while the selection rules for the Raman and infrared have been discussed by Placzek,[3] Tisza[4] and others.

In order to provide a tabular presentation of the important results of these theories for a special class of molecules, so arranged that they may be used without any knowledge of group theory, the degeneracies, number of permitted Raman and infrared fundamentals, and the polarization properties of the Raman lines have been calculated for molecules in which two or more atoms (which may be identical or different) are attached to a single central atom. The treatment is intended to be complete up to six attached atoms; that is, every possible symmetry for such molecules is listed, even those which are not very reasonable physically. For molecules with seven and eight outer atoms, only a few of the more reasonable structures are given, since there are very few molecules of these classes known and a very large number of possible symmetries.

The group-theoretical method used to find the number and degeneracies of the normal vibrations was described in a previous paper,[5] where it was used to obtain the normal coordinates and frequency formulas for benzene. The selection rules have also been obtained by the application of group theory[4] and the results checked wherever possible with the table given by Placzek.[3] (The following divergences from his results were found: p. 81 of the English translation,[6] point group S_{pu}, line labelled B_1, fifth column, read "all zero but C_{xy}"; line labelled B_2, fifth column, "all zero but $C_{xx} = -C_{yy}$"; line labelled C, fifth column, "$C_{xy} = C_{ii} = 0$"; line labelled D, sixth column, "$C_{xx} = -C_{yy}$, $C_{ii} = 0$.")

In using these results in connection with experimentally observed spectra, it is necessary to take certain precautions. Thus the number of Raman lines found may not coincide with that theoretically required for two reasons: first, lines which are not forbidden by symmetry restrictions may still be so weak that they do not appear under ordinary conditions, and second, overtones and combinations may occur in special cases. The latter difficulty is one which is rather frequently observed in spite of the fact that overtones and combinations should be much less important in Raman spectra than in infrared spectra. Another phenomenon which sometimes

[1] C. J. Brester, Kristallsymmetrie und Reststrahlen, Utrecht, 1923; Zeits. f. Physik **24**, 324 (1924).

[2] E. Wigner, Gott. Nach. 133 (1930).

[3] G. Placzek, *Leipziger Vorträge*, p. 71, 1931; Zeits. f. Physik **70**, 84 (1931). G. Placzek and E. Teller, Zeits. f. Physik **81**, 209 (1933).

[4] L. Tisza, Zeits. f. Physik **82**, 48 (1933).

[5] E. Bright Wilson, Jr., Phys. Rev. **45**, 706 (1934).

[6] P. Debye, *The Structure of Molecules*, Blackie and Sons, Ltd., London, 1932.

occurs, for example in CO_2 and CCl_4, and which causes deviations from the simple selection rules, is quantum-mechanical resonance between certain of the energy states of the molecule due to accidental coincidence or approximate coincidence of the levels corresponding to different types of vibration. This effect usually allows otherwise forbidden lines to appear in the spectrum, but it is probably not very common.

Explanation of Tables

The results are given in separate tables, arranged according to the number of atoms in the molecule. Thus Table I lists triatomic molecules of the type AB_2 and ABB′, Table II includes AB_3, AB_2B', and ABB′B″, etc. A is not equivalent by symmetry to any of the B's (although it may be an atom of the same element, as for example in N−N−O).

The numbering, given in the first column of the tables, is designed to indicate the number and character of the attached atoms. The figure in front of the dot gives the total number of attached atoms while the figures following the dot indicate the numbers of symmetrically related atoms. Thus 6.6 means that the molecule is AB_6 in which all six B atoms are equivalent from a symmetry standpoint. 6.42 refers to AB_4B_2', etc. When there are several molecules of the same type but of different symmetries, they are distinguished by using a, b, c, etc. The name, given in the second column, is meant to be descriptive enough to characterize the structure if possible, but in addition the coordinates of the atoms are given under the discussion of each type. The notation R and L following the name of a structure indicates that right and left-handed forms are possible.

The column labelled I gives the point-group symmetry of the structure, the symbols being those of Schönflies,[7] which represent the axes, planes and other elements of symmetry possessed by the molecule. The column headed II tells whether the molecule is a linear rotator L, a spherical top Sp (which has three equal moments of inertia), a symmetric top S (with one distinct and two equal moments of inertia), or an asymmetric top A (which has three unequal moments of inertia).

The columns labelled ν_1, ν_2, ν_3 contain the number of singly, doubly, and triply degenerate normal frequencies of vibration. Only molecules with cubic point-group symmetries can have triply degenerate frequencies. Under R is listed the number of fundamental frequencies of vibration which are allowed to appear in the Raman spectrum, although a line so permitted may be of very small intensity. Following this number, in parentheses, is the number of these Raman fundamentals which have the special depolarization $\rho=\frac{3}{4}$, when plane polarized incident light is used. ρ is the ratio of the intensities of the perpendicular and parallel components of the scattered light. For unpolarized incident light this becomes $\rho=6/7$.

Under I.R. is given the number of fundamental frequencies which are active in the infrared absorption spectra, the figures in parentheses being the number of these bands which are of the || type[8] if the molecule is a symmetric top. Finally, the last column tabulates the symmetries of the possible normal vibrations, the degrees of the factors into which the secular equation for the normal coordinate problem may be factored by the use of the symmetry of the molecule, the degeneracies of these vibrations, and the ones which are active in the Raman and infrared spectra. To illustrate: 2^R, 0, 2^{RI}, 1^R, $2_2{}^{RI}$ after 4.4d means that there are two frequencies with the symmetry of Γ_1 or A_1, the first irreducible representation of the point-group V_d, none with symmetry Γ_2 or A_2, two with Γ_3 or B_2, one with Γ_4 or B_1, and two doubly degenerate frequencies with symmetry Γ_5 or E_1, the degeneracy being indicated by the subscript. The meaning of the term "irreducible representation" is explained in the paper on benzene already referred to.[5] The order Γ_1, Γ_2, etc. is that used by Wigner[2] in his tabulation of the irreducible representations of the crystallographic point groups. Several point groups which do not occur in crystallography were used: namely $D_{\infty h}$, $C_{\infty v}$, D_{5h}, C_{5v}, C_{7h}, C_{7v}, C_{8h}, C_{8v} and D_{4d}, the characters for their irreducible representations being taken from the general tables given by Tisza.[4]

[7] H. Hilton, *Mathematical Crystallography*, Chapters V, VI. Oxford, 1903.

[8] D. M. Dennison, Rev. Mod. Phys. **3**, 314 (1931).

The numbers with superscript R indicate the frequencies which are active in the Raman spectrum while a superscript I on a number means that this frequency is infrared active. The numbers themselves, besides the significance given to them above, also represent the degrees of the factors of the factored secular equation. For the linear molecules, to which Wigner's tables do not apply, the notation of Tisza[4] is used for the irreducible representations.

Discussion of Results

In the discussion of individual cases which is given below, the number and name of the structure is followed by the Cartesian coordinates of the different atoms, with A always at the origin. u, v, w represent parameters which are not fixed by the symmetry, while the letter o has been printed instead of zero. These were mostly taken from a tabulation by Nowacki[9] of the equivalent positions for the point-groups. (Two slight misprints were found in this paper; namely, in Table III, p. 28, after $D_{2d} \equiv V$ (4) the second line should read $|xxz|\bar{x}x\bar{z}|\bar{x}\bar{x}z|x\bar{x}\bar{z}|$ (C_s). After D_{3d} (6) (b) the second line should read $|\bar{x}0x\bar{z}|x\bar{x}0\bar{z}|0x\bar{x}\bar{z}|$ (C_s).) Wherever possible examples are given of molecules which have been found or which might be supposed to belong to the given type. In a number of examples which seem likely to be of importance and which, so far as I know, have not been previously treated, figures are given showing the normal vibrations, derived from the symmetry restrictions yielded by the group theory. The order used in the diagrams is the same as that in the last column of the tables. Only one representative of a set of degenerate vibrations is shown. An example is Fig. 2 which shows the normal vibrations for 5.32a, the trigonal bipyramid model of AB_3B_2'. The last column of Table IV reads: 2^R, 0, 3_2^{RI}; 0, 2^I, 1_2^R. Therefore the first two motions of Fig. 2, labelled ν_1 and ν_2, belong to Γ_1 or A_1', the first irreducible representation of Wigner's table for D_{3h}, and since 2^R has the superscript R, they are Raman active. The next three motions, ν_3', ν_4', ν_5' belong to Γ_3 or E_1'. They are active in both the Raman and infrared spectra and are doubly degenerate; i.e., for each of them there exists another similar motion with the same frequency, differing only in spatial orientation of the directions of motion. The primes on the ν's indicate that to obtain the three true normal vibrations these three motions enclosed in the square brackets must be compounded with proportions determined by the force constants.

Many of the simpler structures listed in Tables I–VII have been previously studied, and although it is impracticable to give all the references it is hoped that those listed will enable the others to be found.

I am very much indebted to Professor Linus Pauling for many valuable suggestions in connection with this paper.

Table I. *Molecules with three atoms.*

No.	Name	I	II	ν_1	ν_2	R	I.R.	Irreducible representations
2.2a	Symmetrical collinear	$D_{\infty h}$	L	2	1	1(0)	2	A_{1g}^R, A_{2u}^I, $E_{1u}^I(2)$.
2.2b	Symmetrical bent	C_{2v}	A	3		3(1)	3	2^{RI}, 0, 0, 1^{RI}.
2.11a	Unsymmetrical collinear	$C_{\infty v}$	L	2	1	3(1)	3	$2A_1^{RI}$, $E_1^{RI}(2)$.
2.11b	Unsymmetrical bent	C_s	A	3		3(0)	3	3^{RI}, 0.

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2.2a. Symmetrical collinear. B : oow, oo$\bar{w}$. CO_2,[10, 11] CS_2.[10, 12] Normal coordinates.[10]

2.2b. Symmetrical bent. B : uow, $\bar{u}$ow. H_2O,[10] SO_2,[10] H_2S.[10] Normal coordinates.[10]

2.11a. Unsymmetrical collinear. B : oow. B′ : oow′. N_2O,[10, 13] COS.[14] Normal coordinates.[10]

2.11b. Unsymmetrical bent. B : uow. B′ : u′ow′. H^1H^2O,[15] H^1H^2S. Normal coordinates.[10, 16]

[9] W. Nowacki, Zeits. f. Kristallographie (A) **86**, 19 (1933).

[10] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt*, Springer, Berlin, 1931, pp. 169–186.

[11] A. Adel and D. M. Dennison, Phys. Rev. **44**, 99 (1933).

[12] G. Placzek, reference 6, p. 88.

[13] E. K. Plyler and E. F. Barker, Phys. Rev. **38**, 1827 (1931).

[14] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. **A135**, 375 (1932).

[15] R. W. Wood, Nature **132**, 970 (1933).

[16] P. C. Cross and J. H. Van Vleck, J. Chem. Phys. **1**, 350 (1933).

TABLE II. *Molecules with four atoms.*

No.	Name	I	II	ν_1	ν_2	R	I.R.	Irreducible representations
3.3a	Plane equilateral triangle	D_{3h}	S	2	2	3(2)	3(1)	1^R, 0, $2_2{}^{RI}$; 0, 1^I, 0.
3.3b	Regular pyramid	C_{3v}	S	2	2	4(2)	4(2)	2^{RI}, 0, $2_2{}^{RI}$.
3.21a	Plane isosceles triangle	C_{2v}	A	6		6(3)	6	3^{RI}, 1^{RI}, 0, 2^{RI}.
3.21b	Pyramid	C_s	A	6		6(2)	6	4^{RI}, 2^{RI}.
3.111a	Linear	$C_{\infty v}$	L	3	2	5(2)	5	$3A_1{}^{RI}$, $2E_1{}^{RI}(2)$.
3.111b	Plane scalene triangle	C_s	A	6		6(1)	6	5^{RI}, 1^{RI}.
3.111c	Pyramid (R+L)	C_1	A	6		6(0)	6	6^{RI}.

MOLECULES WITH FOUR ATOMS

3.3a. Plane equilateral triangle. B : (ovo)$(\frac{1}{2}\sqrt{3}\text{v}, -\frac{1}{2}\text{v}, \text{o})(-\frac{1}{2}\sqrt{3}\text{v}, -\frac{1}{2}\text{v}, \text{o})$. $CO_3{}^{--}$,[17] $NO_3{}^-$.[17] Normal coordinates.[17, 18]

3.3b. Regular pyramid. B : (o, v, w)$(\frac{1}{2}\sqrt{3}\text{v}, -\frac{1}{2}\text{v}, \text{w})(-\frac{1}{2}\sqrt{3}\text{v}, -\frac{1}{2}\text{v}, \text{w})$. NH_3,[19] $AsCl_3$,[17, 20] PCl_3,[17, 20] AsF_3,[20] etc.[21] Normal coordinates.[17]

3.21a. Plane isosceles triangle. B : uvo, ūvo. B′ : ov′o. H_2CO.[22] Approximate normal coordinates.[22, 23]

3.21b. Pyramid with isosceles base. B : uvw, ūvw. B′ : ov′w′. PCl_2Br,[24] $PClBr_2$,[24] NH_2Cl.

3.111a. Linear. B : oow. B′ : oow′. B″ : oow″.

3.111b. Plane scalene triangle. B : uvo. B′ : u′v′o. B″ : u″v″o. H^1H^2CO.

3.111c. Pyramid with scalene base. B : uvw. B′ : u′v′w′. B″ : u″v″w″.

TABLE III. *Molecules with five atoms.*

No.	Name	I	II	ν_1	ν_2	ν_3	R	I.R.	Irreducible representations
4.4a	Regular tetrahedron	T_d	Sp	1	1	2	4(3)	2	1^R, 0, $1_2{}^R$, $2_3{}^{RI}$, 0.
4.4b	Plane square	D_{4h}	S	5	2		3(2)	3(1)	1^R, 0, 1^R, 1^R, 0; 0, 1^I, 0, 1, $2_2{}^I$.
4.4c	Square pyramid	C_{4v}	S	5	2		7(5)	4(2)	2^{RI}, 0, 2^R, 1^R, $2_2{}^{RI}$.
4.4d	Tetragonal sphenoid	V_d	S	5	2		7(5)	4(2)	2^R, 0, 2^{RI}, 1^R, $2_2{}^{RI}$.
4.4e	Plane rectangle	V_h	A	9			3(1)	5	2^R, 0, 1^R, 0; 1, 2^I, 1^I, 2^I.
4.4f	Orthorhombic sphenoid (R+L)	V	A	9			9(6)	6	3^R, 2^{RI}, 2^{RI}, 2^{RI}.
4.4g	Rectangular pyramid	C_{2v}	A	9			9(6)	7	3^{RI}, 2^{RI}, 2^R, 2^{RI}.
4.31a	Trigonal pyramid	C_{3v}	S	3	3		6(3)	6(3)	3^{RI}, 0, $3_2{}^{RI}$.
4.22a	Linear	$D_{\infty h}$	L	4	3		3(1)	4	$2A_{1g}{}^R$, $2A_{2u}{}^I$, $E_{1g}{}^R(2)$, $2E_{1u}{}^I(2)$.
4.22b	Plane rhombus	V_h	A	9			3(1)	6	2^R, 0, 1^R, 0; 0, 2^I, 2^I, 2^I.
4.22c	Plane trapezoid	C_{2v}	A	9			9(5)	8	4^{RI}, 1^{RI}, 1^R, 3^{RI}.
4.22d	Rhombic pyramid	C_{2v}	A	9			9(5)	8	4^{RI}, 2^{RI}, 1^R, 2^{RI}.
4.22e	Plane parallelogram	C_{2h}	A	9			3(0)	6	3^R, 0, 2^I, 4^I.
4.22f	Trapezoidal pyramid	C_s	A	9			9(4)	9	5^{RI}, 4^{RI}.
4.22g	Monoclinic sphenoid (R+L)	C_2	A	9			9(4)	9	5^{RI}, 4^{RI}.
4.211a	Plane	C_{2v}	A	9			9(5)	9	4^{RI}, 2^{RI}, 0, 3^{RI}.
4.211b	Monoclinic sphenoid	C_s	A	9			9(3)	9	6^{RI}, 3^{RI}.
4.1111a	Linear	$C_{\infty v}$	L	4	3		7(3)	7	$4A_1{}^{RI}$, $3E_1{}^{RI}(2)$.
4.1111b	Plane	C_s	A	9			9(2)	9	7^{RI}, 2^{RI}.
4.1111c	General (R+L)	C_1	A	9			9(0)	9	9^{RI}.

MOLECULES WITH FIVE ATOMS

4.4a. Regular tetrahedron. B : www, w̄ww̄, w̄w̄w, ww̄w̄. CCl_4,[25] CBr_4,[25] $SiCl_4$,[25] etc. Normal coordinates.[25, 26]

4.4b. Plane square. B : woo, owo, w̄oo, ow̄o. $PtCl_4{}^{--}$, $PdCl_4{}^{--}$.

4.4c. Pyramid with square base. B : wov, owv, w̄ov, ow̄v. SCl_4, $TeCl_4$. Normal coordinates.[27]

4.4d. Tetragonal sphenoid. B : wwv, w̄wv̄, w̄w̄v, ww̄v̄.

4.4e. Plane rectangle. B : uvo, ūv̄o, ūvo, uv̄o.

4.4f. Orthorhombic sphenoid. B : uvw, uv̄w̄, ūvw̄, ūv̄w.

4.4g. Pyramid with rectangular base. B : uvw, ūv̄w, ūvw, uv̄w.

4.31. Trigonal pyramid. B : (o, v, w)$(\frac{1}{2}\sqrt{3}\text{v}, -\frac{1}{2}\text{v}, \text{w})(-\frac{1}{2}\sqrt{3}\text{v}, -\frac{1}{2}\text{v}, \text{w})$. B′ : oow′. CH_3Cl,[28] CH_3Br,[28] etc.

[17] Kohlrausch, reference 10, pp. 195–205.

[18] H. H. Nielsen, Phys. Rev. **32**, 773 (1928).

[19] C. M. Lewis and W. V. Houston, Phys. Rev. **44**, 903 (1933).

[20] D. M. Yost and J. E. Sherborne, J. Chem. Phys. **2**, 125 (1934).

[21] J. H. Hibben, Chem. Rev. **13**, 345 (1933).

[22] Kohlrausch, reference 10, pp. 211–212.

[23] F. Matossi and H. Aderhold, Zeits. f. Physik **68**, 683 (1931).

[24] B. Trumpy, Zeits. f. Physik **68**, 675 (1931).

[25] Kohlrausch, reference 10, pp. 212–218.

[26] D. M. Yost, C. C. Steffens and S. T. Gross, J. Chem. Phys. **2**, 311 (1934).

[27] V. Guillemin, Ann. d. Physik **81**, 173 (1926).

[28] Kohlrausch, reference 10, p. 208.

4.22a. Linear. B : oow, oo$\bar{w}$. B′ : oow′, oo$\bar{w}$′. C_3O_2.[29]

4.22b. Plane rhombus. B : uoo, $\bar{u}$oo. B′ : ov′o, o$\bar{v}$′o.

4.22c. Plane regular trapezoid. B : uvo, $\bar{u}$vo. B′ : u′v′o, $\bar{u}$′v′o.

4.22d. Rhombic pyramid. B : uow, $\bar{u}$ow. B′ : ov′w′, o$\bar{v}$′w′. If the two B′ atoms are placed above A with 2B below, this structure is a distorted tetrahedron. CH_2Cl_2,[30] CF_2Cl_2.[31]

4.22e. Plane parallelogram. B : uvo, $\bar{u}\bar{v}$o. B′ : u′v′o, $\bar{u}$′$\bar{v}$′o.

4.22f. Pyramid with trapezoidal base. B : uvw, $\bar{u}$vw. B′ : u′v′w′, $\bar{u}$′v′w′.

4.22g. Monoclinic sphenoid. B : uvw, $\bar{u}\bar{v}$w. B′ : u′v′w′, $\bar{u}$′$\bar{v}$′w′. If B and B′ are on same side of A this is a pyramid with a parallelogram for a base.

4.211a. Plane. B : uow, $\bar{u}$ow. B′ : oow′. B″ : oow″. CH_2CO.

4.211b. Monoclinic sphenoid. B : uvw, uv$\bar{w}$. B′ : u′v′o. B″ : u″v″o. $CHFCl_2$.[31]

4.1111a. Linear. B : oow. B′ : oow′. B″ : oow″. B‴oow‴.

4.1111b. Plane. B : uvo. B′ : u′v′o. B″ : u″v″o. B‴ : u‴v‴o.

4.1111c. General. No symmetry.

TABLE IV. *Molecules with six atoms.*

No.	Name	I	II	ν_1	ν_2	R	I.R.	Irreducible representations
5.5a	Plane pentagon	D_{5h}	S	2	5	3(2)	3(1)	1^R, 0, $2_2{}^I$, $2_2{}^R$; 1^I, 0, 0, 1_2.
5.5b	Pentagonal pyramid	C_{5v}	S	2	5	7(5)	4(2)	2^{RI}, 0, $2_2{}^{RI}$, $3_2{}^R$.
5.41a	Square pyramid	C_{4v}	S	6	3	9(6)	6(3)	3^{RI}, 0, 2^R, 1^R, $3_2{}^{RI}$.
5.41b	Rectangular pyramid	C_{2v}	A	12		12(8)	10	4^{RI}, 3^{RI}, 2^R, 3^{RI}.
5.32a	Trigonal bipyramid	D_{3h}	S	4	4	6(4)	5(2)	2^R, 0, $3_2{}^{RI}$; 0, 2^I, $1_2{}^R$.
5.311a	Polar trigonal bipyramid	C_{3v}	S	4	4	8(4)	8(4)	4^{RI}, 0, $4_2{}^{RI}$.
5.221a	Plane	C_{2v}	A	12		12(7)	11	5^{RI}, 4^{RI}, 1^R, 2^{RI}.
5.221b	Triangular bipyramid	C_{2v}	A	12		12(7)	11	5^{RI}, 3^{RI}, 1^R, 3^{RI}.
5.221c	Trapezoidal pyramid	C_s	A	12		12(5)	12	7^{RI}, 5^{RI}.
5.221d	(R+L)	C_2	A	12		12(6)	12	6^{RI}, 6^{RI}.
5.2111a	Triangular bipyramid	C_s	A	12		12(4)	12	8^{RI}, 4^{RI}.
5.11111a	Linear	$C_{\infty v}$	L	5	4	9(4)	9	$5A_1{}^{RI}$, $4E_1{}^{RI}(2)$.
5.11111b	Plane	C_s	A	12		12(3)	12	9^{RI}, 3^{RI}.
5.11111c	General (R+L)	C_1	A	12		12(0)	12	12^{RI}.

MOLECULES WITH SIX ATOMS

5.5a. Plane pentagon. B : (o, v, o)(av, bv, o)(cv, −dv, o)(−cv, −dv, o)(−av, bv, o). Here a=sin 72°, b=cos 72°, c=sin 36°, d=cos 36°.

5.5b. Pentagonal pyramid. B : (o, v, w)(av, bv, w)(cv, −dv, w)(−cv, −dv, w)(−av, bv, w). a, b, c, d as in 5.5a.

5.41a. Square pyramid. B : uuw, u$\bar{u}$w, $\bar{u}\bar{u}$w, $\bar{u}$uw. B′ : oow′. PF_5.[32] Modes of vibration, Fig. 1.

5.41b. Rectangular pyramid. B : uvw, $\bar{u}\bar{v}$w, $\bar{u}$vw, u$\bar{v}$w. B′ : oow′.

5.32a. Trigonal bipyramid. B : (o, v, o)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o). B′ : (oow′)(oo$\bar{w}$′). PF_3Cl_2. Modes of vibration, Fig. 2.

5.311a. Polar trigonal bipyramid. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w). B′ : (oow′). B″ : (oow″). PF_3ClI, CH_3CN.

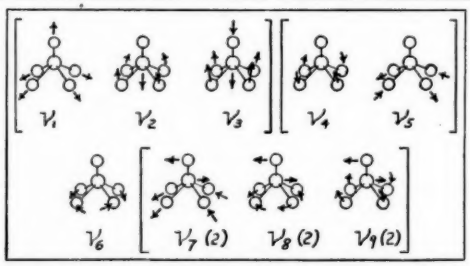

FIG. 1. Modes of vibration of 5.41a, square pyramid. Bracketed motions must be combined to give true modes.

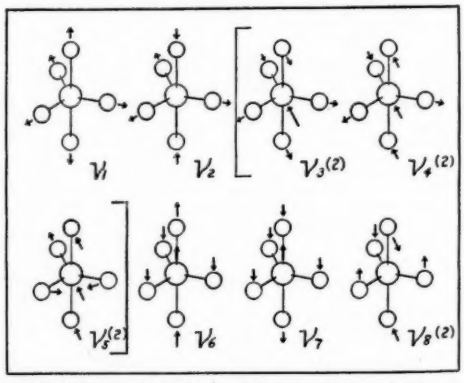

FIG. 2. Modes of vibration of 5.32a, trigonal bipyramid. Bracketed motions must be combined to give true modes.

[29] L. O. Brockway and Linus Pauling, Proc. Nat. Acad. Sci. **19**, 860 (1933).

[30] Kohlrausch, reference 10, p. 305.

[31] C. A. Bradley, Jr., Phys. Rev. **40**, 908 (1932).

[32] L. O. Brockway. Private communication. Electron diffraction studies give this structure for PF_5.

5.221a. Plane. B : uow, ūow. B′ : u′ow′, ū′ow′. B″ : oow″.

5.221b. Triangular bipyramid. B : uow, ūow. B′ : ov′w′, ov̄′w′. B″ : oow″.

5.221c. Trapezoidal pyramid. B : uvw, uvw̄. B′ : u′v′w′, u′v′w̄′. B″ : u″v″o.

5.221d. B : uvw, ūv̄w. B′ : u′v′w′, ū′v̄′w′. B″ : oow″.

5.2111a. Triangular bipyramid. B : uvw, uvw̄. B′ : u′v′o. B″ : u″v″o. B‴ : u‴v‴o.

5.11111a. Linear. $B^{(i)}$: oow_i.

5.11111b. Plane. $B^{(i)}$: u_iv_io.

5.11111c. General. No symmetry.

TABLE V. *Molecules with seven atoms.*

No.	Name		I	II	ν_1	ν_2	ν_3	R	I.R.	Irreducible representations
6.6a	Regular octahedron		O_h	Sp	1	1	4	3(2)	2	1^R, 0, 1_2^R, 1_3^R, 0; 0, 0, 0, 1_3, 2_3^I.
6.6b	Regular plane hexagon		D_{6h}	S	5	5		3(2)	3(1)	1^R, 0, 0, 1, 2_2^R, 0; 0, 1^I, 1, 1, 1_2, 2_2^I.
6.6c	Hexagonal pyramid		C_{6v}	S	5	5		7(5)	4(2)	2^{RI}, 0, 2, 1, 3_2^R, 2_2^{RI}.
6.6d	Trigonal prism		D_{3h}	S	5	5		7(5)	5(2)	2^R, 0, 3_2^{RI}; 1, 2^I, 2_2^R.
6.6e	Trigonal plane hexagon		D_{3h}	S	5	5		7(5)	5(1)	2^R, 1, 4_2^{RI}; 1, 1^I, 1_2^R.
6.6f	Twisted trigonal prism		D_{3d}	S	5	5		4(2)	5(2)	2^R, 0, 2_2^R; 2^I, 1, 3_2^I.
6.6g	Twisted trigonal prism	(R+L)	D_3	S	5	5		8(5)	7(2)	3^R, 2^I, 5_2^{RI}.
6.6h	Trigonal hexangular pyramid		C_{3v}	S	5	5		8(5)	8(3)	3^{RI}, 2, 5_2^{RI}.
6.51a	Pentagonal pyramid		C_{5v}	S	3	6		9(6)	6(3)	3^{RI}, 0, 3_2^{RI}, 3_2^R.
6.42a	Tetragonal octahedron		D_{4h}	S	7	4		5(3)	5(2)	2^R, 0, 1^R, 1^R, 1_2^R; 0, 2^I, 0, 1, 3_2^I.
6.42b			Vd	S	7	4		11(8)	7(3)	3^R, 0, 3^{RI}, 1^R, 4_2^{RI}.
6.42c	Rectangular bipyramid		V_h	A	15			6(3)	8	3^R, 1^R, 1^R, 1^R; 1, 3^I, 2^I, 3^I.
6.42d	Plane		V_h	A	15			6(3)	8	3^R, 1^R, 2^R, 0; 1, 3^I, 2^I, 3^I.
6.42e		(R+L)	V	A	15			15(11)	11	4^R, 4^{RI}, 3^{RI}, 4^{RI}.
6.42f			C_{2v}	A	15			15(10)	12	5^{RI}, 3^{RI}, 3^R, 4^{RI}.
6.42g			C_{2h}	A	15			6(2)	9	4^R, 2^R, 4^I, 5^I.
6.411a	Polar tetragonal octahedron		C_{4v}	S	7	4		11(7)	8(4)	4^{RI}, 0, 2^R, 1^R, 4_2^{RI}.
6.411b	Polar rectangular bipyramid		C_{2v}	A	15			15(10)	13	5^{RI}, 4^{RI}, 2^R, 4^{RI}.
6.33a	Plane		D_{3h}	S	5	5		7(5)	6(2)	2^R, 1, 4_2^{RI}; 0, 2^I, 1_2^R.
6.33b	Plane		C_{3h}	S	5	5		8(5)	6(2)	3^R, 4^{RI}, 4^{RI}; 2^I, 1^R, 1^R.
6.33c	Pyramid or prism		C_{3v}	S	5	5		9(5)	9(4)	4^{RI}, 1, 5_2^{RI}.
6.33d	Pyramid or prism	(R+L)	C_3	S	5	5		10(5)	10(5)	5^{RI}, 5^{RI}, 5^{RI}.
6.3111a	Trigonal bipyramid		C_{3v}	S	5	5		10(5)	10(5)	5^{RI}, 0, 5_2^{RI}.
6.222a	Linear		$D_{\infty h}$	L	6	5		5(2)	6	$3A_{1g}^R$, $3A_{2u}^I$, $3E_{1u}^I$, $2E_{1g}^R$.
6.222b	Orthorhombic octahedron		V_h	A	15			6(3)	9	3^R, 1^R, 1^R, 1^R; 0, 3^I, 3^I, 3^I.
6.222c	Trapezoidal bipyramid		C_{2v}	A	15			15(9)	13	6^{RI}, 4^{RI}, 2^R, 3^{RI}.
6.222d	Plane		C_{2h}	A	15			6(1)	9	5^R, 1^R; 3^I, 6^I.
6.222e	Monoclinic octahedron		C_{2h}	A	15			6(2)	9	4^R, 2^R, 3^I, 6^I.
6.222f	Triangular prism		C_s	A	15			15(7)	15	8^{RI}, 7^{RI}.
6.222g	Monoclinic octahedron	(R+L)	C_2	A	15			15(7)	15	8^{RI}, 7^{RI}.
6.222h	Triclinic octahedron		C_i	A	15			o(0)	9	6^R, 9^I.
6.2211a	Orthorhombic octahedron		C_{2v}	A	15			15(9)	14	6^{RI}, 4^{RI}, 1^R, 4^{RI}.
6.2211b	Heptahedron		C_s	A	15			15(6)	15	9^{RI}, 6^{RI}.
6.2211c	Monoclinic octahedron	(R+L)	C_2	A	15			15(8)	15	7^{RI}, 8^{RI}.
6.21111a			C_s	A	15			15(5)	15	10^{RI}, 5^{RI}.
6.111111a	Linear		$C_{\infty v}$	L	6	5		11(5)	11	$6A_1^{RI}$, $5E_1^{RI}$.
6.111111b	Plane		C_s	A	15			15(4)	15	11^{RI}, 4^{RI}.
6.111111c	General		C_1	A	15			15(0)	15	15^{RI}.

MOLECULES WITH SEVEN ATOMS

6.6a. Regular octahedron. B : uoo, ūoo, ouo, oūo, oou, ooū. SF_6[26], SeF_6[26], TeF_6[26]. Modes of vibration, Fig. 3. Normal frequencies.[26]

6.6b. Regular plane hexagon. B : (o, v, o)($\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, o)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o)(o, v̄, o)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o)($-\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, o).

6.6c. Hexagonal pyramid. B : (ovw)($\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)(o, v̄, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, w).

6.6d. Trigonal prism. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)(o, v, w̄)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w̄)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v,w̄).

6.6e. Trigonal plane hexagon. B : (ū, v, o)(u, v, o)($\frac{1}{2}\sqrt{3}$v+$\frac{1}{2}$u, $-\frac{1}{2}$v+$\frac{1}{2}\sqrt{3}$u, o)($\frac{1}{2}\sqrt{3}$v−$\frac{1}{2}$u, $-\frac{1}{2}$v $-\frac{1}{2}\sqrt{3}$u, o)($-\frac{1}{2}\sqrt{3}$v+$\frac{1}{2}$u, $-\frac{1}{2}$v−$\frac{1}{2}\sqrt{3}$u, o)($-\frac{1}{2}\sqrt{3}$v−$\frac{1}{2}$u, $-\frac{1}{2}$v+$\frac{1}{2}\sqrt{3}$u, o).

6.6f. Twisted trigonal prism. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)(o, v̄, w̄)($-\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, w̄)($\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, w̄).

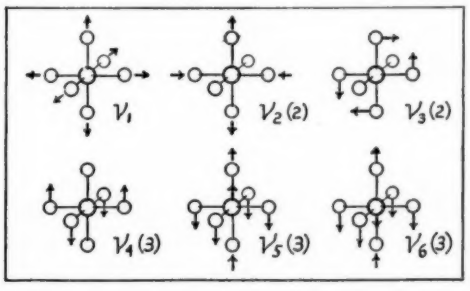

FIG. 3. Modes of vibration of 6.6a, regular octahedron.

6.6g. Twisted trigonal prism. B : (ū, v, w)(u, v, w̄)($\frac{1}{2}\sqrt{3}$v+$\frac{1}{2}$u, $-\frac{1}{2}$v+$\frac{1}{2}\sqrt{3}$u, w)($\frac{1}{2}\sqrt{3}$v−$\frac{1}{2}$u, $-\frac{1}{2}$v−$\frac{1}{2}\sqrt{3}$u, w̄)($-\frac{1}{2}\sqrt{3}$v+$\frac{1}{2}$u, $-\frac{1}{2}$v−$\frac{1}{2}\sqrt{3}$u, w)($-\frac{1}{2}\sqrt{3}$v−$\frac{1}{2}$u, $-\frac{1}{2}$v+$\frac{1}{2}\sqrt{3}$u, w̄).

6.6h. Trigonal hexangular pyramid. B : (ū, v, w)(u, v, w)($\frac{1}{2}\sqrt{3}$v+$\frac{1}{2}$u, $-\frac{1}{2}$v+$\frac{1}{2}\sqrt{3}$u, w)($\frac{1}{2}\sqrt{3}$v −$\frac{1}{2}$u, $-\frac{1}{2}$v−$\frac{1}{2}\sqrt{3}$u, w)($-\frac{1}{2}\sqrt{3}$v+$\frac{1}{2}$u, $-\frac{1}{2}$v −$\frac{1}{2}\sqrt{3}$u, w)($-\frac{1}{2}\sqrt{3}$v−$\frac{1}{2}$u, $-\frac{1}{2}$v+$\frac{1}{2}\sqrt{3}$u, w).

6.51a. Pentagonal pyramid. B : (o, v, w)(av, bv, w)(cv, −dv, w)(−cv, −dv, w)(−av, bv, w). B′ : (oow′). a, b, c, d as in 5.5a.

6.42a. Tetragonal octahedron. B : uoo, ūoo, ouo, oūo. B′ : oou′, ooū′.

6.42b. B : uow, ūow, ouw̄, oūw̄. B′ : oow′, oow̄′.

6.42c. Rectangular bipyramid. B : uvo, ūv̄o, ūvo, uv̄o. B′ : oow′, oow̄′.

6.42d. Plane. B : uvo, ūv̄o, ūvo, uv̄o. B′ : u′oo, ū′oo.

6.42e. B : uvw, uv̄w̄, ūvw̄, ūv̄w. B′ : oow′, oow̄′.

6.42f. B : uvw, uv̄w, ūv̄w, ūvw. B′ : u′ow′, ū′ow′. $(CH_2)_2O$.

6.42g. B : uvw, uv̄w, ūv̄w̄, ūvw̄. B′ : u′ow′, ū′ow̄′.

6.411a. Polar tetragonal octahedron. B : uow, ūow, ouw, oūw. B′ : oow′. B″ : oow″.

6.411b. Polar rectangular bipyramid. B : uvw, ūv̄w, ūvw, uv̄w. B′ : oow′. B″ : oow″.

6.33a. Plane. B : (o, v, o)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o). B′ : (o, v̄, o)($-\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, o)($\frac{1}{2}\sqrt{3}$v, $\frac{1}{2}$v, o).

6.33b. Plane. B : (o, v, o)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, o). B′ : (u′, v′, o)($\frac{1}{2}\sqrt{3}$v′−$\frac{1}{2}$u′, $-\frac{1}{2}$v′ −$\frac{1}{2}\sqrt{3}$u′, o)($-\frac{1}{2}\sqrt{3}$v′−$\frac{1}{2}$u′, $-\frac{1}{2}$v′+$\frac{1}{2}\sqrt{3}$u′, o).

6.33c. Pyramid or prism. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w). B′ : (o, v′, w′)($\frac{1}{2}\sqrt{3}$v′, $-\frac{1}{2}$v′, w′)($-\frac{1}{2}\sqrt{3}$v′, $-\frac{1}{2}$v′, w′).

6.33d. Pyramid or prism. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w). B′ : (u′, v′, w′)($\frac{1}{2}\sqrt{3}$v′−$\frac{1}{2}$u′, $-\frac{1}{2}$v′−$\frac{1}{2}\sqrt{3}$u′, w′)($-\frac{1}{2}\sqrt{3}$v′ −$\frac{1}{2}$u′, $-\frac{1}{2}$v′+$\frac{1}{2}\sqrt{3}$u′, w′).

6.3111a. Trigonal bipyramid. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w). B′ : oow′. B″ : oow″. B‴ : oow‴. CH_3NCO.

6.222a. Linear. B : oow, oow̄. B′ : oow′, oow̄′. B″ : oow″, oow̄″.

6.222b. Orthorhombic octahedron. B : uoo, ūoo. B′ : ov′o, ov̄′o. B″ : oow″, oow̄″.

6.222c. Trapezoidal bipyramid. B : uow, ūow. B′ : u′ow′, ū′ow′. B″ : ov″w″, ov̄″w″.

6.222d. Plane. B : uvo, ūv̄o. B′ : u′v′o, ū′v̄′o. B″ : u″v″o, ū″v̄″o.

6.222e. Monoclinic octahedron. B : uvo, ūv̄o. B′ : u′v′o, ū′v̄′o. B″ : oow″, oow̄″.

6.222f. Triangular prism. B : uvw, uvw̄. B′ : u′v′w′, u′v′w̄′. B″ : u″v″w″, u″v″w̄″.

6.222g. Monoclinic octahedron. B : uvw, ūv̄w. B′ : u′v′w′, ū′v̄′w′. B″ : u″v″w″, ū″v̄″w″.

6.222h. Triclinic octahedron. B : uvw, ūv̄w̄. B′ : u′v′w′, ū′v̄′w̄′. B″ : u″v″w″, ū″v̄″w̄″.

6.2211a. Orthorhombic octahedron. B : uow, ūow. B′ : ov′w′, ov̄′w′. B″ : oow″. B‴ : oow‴.

6.2211b. Heptahedron. B : uvw, uvw̄. B′ : u′v′w′, u′v′w̄′. B″ : u″v″o. B‴ : u‴v‴o.

6.2211c. Monoclinic octahedron. B : uvw, ūv̄w. B′ : u′v′w′, ū′v̄′w′. B″ : oow″. B‴oow‴.

6.21111a. B : uvw, uvw̄. B′ : u′v′o. B″ : u″v″o. B‴ : u‴v‴o. B⁗ : u⁗v⁗o.

6.111111a. Linear. $B^{(i)}$: oow_i.

6.111111b. Plane. $B^{(i)}$: u_iv_io.

6.111111c. General. No symmetry. $B^{(i)}$: $u_iv_iw_i$.

TABLE VI. *Molecules with eight atoms.*

No.	Name	I	II	ν_1	ν_2	R	I.R.	Irreducible representations
7.7a	Plane heptagon	D_{7h}	S	2	8	3(2)	3(1)	1^R, 0, 2_2^I, 2_2^R, 2_2; 0, 1^I, 0, 1_2, 1_2.
7.7b	Heptagonal pyramid	C_{7v}	S	2	8	7(5)	4(2)	2^{RI}, 0, 2_2^{RI}, 3_2^R, 3_2.
7.52a	Pentagonal bipyramid	D_{5h}	S	4	7	5(3)	5(2)	2^R, 0, 3_2^I, 2_2^R; 2^I, 0, 1_2^R, 1_2.
7.331a		C_{3v}	S	6	6	11(6)	11(5)	5^{RI}, 1, 6_2^{RI}.
7.331b	Truncated trigonal bipyramid	C_{3v}	S	6	6	11(6)	11(5)	5^{RI}, 1, 6_2^{RI}.
7.421a		C_{2v}	A	18		18(12)	15	6^{RI}, 5^{RI}, 3^R, 4^{RI}.

MOLECULES WITH EIGHT ATOMS

Only the type AB_7 is treated completely; the other structures listed were chosen because they seem the most probable physically. IF_7 presumably belongs to one of the classes below.

7.7a. Plane heptagon. B : (o, v, o)(gv, hv, o)(jv, kv, o)(ev, fv, o)(−ev, fv, o)(−jv, kv, o)(−gv, hv, o). g = sin φ, h = cos φ, j = sin 2φ, k = cos 2φ, e = sin 3φ, f = cos 3φ. φ = 2π/7.

7.7b. Heptagonal pyramid. B : (o, v, w)(gv, hv,

w)(jv, kv, w)(ev, fv, w)(−ev, fv, w)(−jv, kv, w)(−gv, hv, w). g, h, j, k, e, f as in 7.7a.

7.52a. Pentagonal bipyramid. B : (o, v, o)(av, bv, o)(cv, −dv, o)(−cv, −dv, o)(−av, bv, o). B′ : (oow′)(oow̄′).

7.331a, b. B : (o, v, w)($\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w)($-\frac{1}{2}\sqrt{3}$v, $-\frac{1}{2}$v, w). B′ : (o, v′, w′)($\frac{1}{2}\sqrt{3}$v′, $-\frac{1}{2}$v′, w′)($-\frac{1}{2}\sqrt{3}$v′, $-\frac{1}{2}$v′, w′). B″ : oow″.

7.421a. B : uvw, ūv̄w, ūvw, uv̄w. B′ : u′ow′, ū′ow′. B″ : oow″.

TABLE VII. *Molecules with nine atoms.*

No.	Name	I	II	ν_1	ν_2	ν_3	R	I.R.	Irreducible representations
8.8a	Cube	O_h	Sp	2	2	5	4(3)	2	1^R, 0, $1_2{}^R$, $2_3{}^R$, 0; 0, 1, 1_2, 1_3, $2_3{}^I$.
8.8b	Plane octagon	D_{8h}	S	5	8		4(3)	3(1)	1^R, 0, 1, 1, $1_2{}^R$, 0, $2_2{}^R$; 0, 1^I, 0, 1, $2_2{}^I$, 2_2, 1_2.
8.8c	Octagonal pyramid	C_{8v}	S	5	8		7(5)	4(2)	2^{RI}, 0, 1, 2, $2_2{}^{RI}$, 3_2, $3_2{}^R$.
8.8d	Archimedian anti-prism	D_{4d}	S	5	8		7(5)	5(2)	2^R, 0, 1, 2^I, $3_2{}^I$, $2_2{}^R$, $3_2{}^R$.
8.8e	Plane tetragonal octagon	D_{4h}	S	11	5		7(5)	5(1)	2^R, 1, 2^R, 2^R, $1_2{}^R$; 1, 1^I, 1, 1, $4_2{}^I$.
8.8f	Tetragonal parallelopiped	D_{4h}	S	11	5		7(5)	5(2)	2^R, 0, 1^R, 2^R, $2_2{}^R$; 1, 2^I, 2, 1, $3_2{}^I$.
8.8g	Twisted cube	D_4	S	11	5		14(11)	7(2)	3^R, 2^I, 3^R, 3^R, $5_2{}^{RI}$.
8.8h	Tetragonal pyramid	C_{4v}	S	11	5		14(11)	8(3)	3^{RI}, 2, 3^R, 3^R, $5_2{}^{RI}$.
8.8i	Twisted tetragonal parallelopiped	V_d	S	11	5		14(11)	8(3)	3^R, 2, 3^{RI}, 3^R, $5_2{}^{RI}$.
8.8j	Rectangular parallelopiped	V_h	A	21			9(6)	9	3^R, 2^R, 2^R, 2^R; 3, 3^I, 3^I, 3^I.

MOLECULES WITH NINE ATOMS

Only the type AB_8 is considered. OsF_8[33] is said to belong to 8.8a or 8.8d.

8.8a. Cube. B : uuu, ūūū, ūuū, uūu, ūūu, uuū, uūū, ūuu.

8.8b. Plane octagon. B : (o, v, o)(mv, mv, o)(v, o, o)(mv, −mv, o)(o, v̄, o)(−mv, −mv, o)(v̄, o, o)(−mv, mv, o). m=$\frac{1}{2}\sqrt{2}$.

8.8c. Octahedral pyramid. B : (o, v, w)(mv, mv, w)(v, o, w)(mv, −mv, w)(o, v̄, w)(−mv, −mv, w)(v̄, o, w)(−mv, mv, w). m=$\frac{1}{2}\sqrt{2}$.

8.8d. Archimedian anti-prism. B : (uuw)(ūūw)(ūuw)(uūw)(pu, o, w̄)(o, pū, w̄)(pū, o, w̄)(o, pu, w̄). p=$\sqrt{2}$.

8.8e. Plane tetragonal octagon. B : uvo, ūv̄o, ūvo, uv̄o, vūo, v̄uo, vuo, v̄ūo.

8.8f. Tetragonal parallelopiped. B : uow, ūow̄, ūow, uow̄, oūw, ouw, ouw̄, oūw̄.

8.8g. Twisted cube. B : uvw, ūvw̄, ūv̄w, uv̄w̄, vūw, v̄uw, vuw̄, v̄ūw̄.

8.8h. Tetragonal octangular pyramid. B : uvw, ūv̄w, ūvw, uv̄w, vūw, v̄uw, vuw, v̄ūw.

8.8i. Twisted tetragonal parallelopiped. B : uvw, ūvw̄, ūv̄w, uv̄w̄, vūw̄, v̄uw̄, vuw, v̄ūw.

8.8j. Rectangular parallelopiped. B : uvw, ūv̄w̄, ūvw̄, uv̄w, ūv̄w, uvw̄, uv̄w̄, ūvw.

[33] H. Braune and S. Knoke, Naturwiss. **21**, 349 (1933).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Some Heat Capacity Data for Liquid Nitrobenzene; No Indication of Allotropy

The suggestion that nitrobenzene exists in two different liquid forms with a transition point at about 9.6°C has been made by Mazur and his collaborators.[1] They have published experimental data which indicate that the density and dielectric constant show discontinuities in the neighborhood of this temperature and from a heating curve they have estimated the heat of transition to be 0.14 calorie per gram. They also state that the heat capacity of the liquid below 9.6° is considerably less than that above this temperature. Other investigators,[2] however, have failed to find evidence of such discontinuities in studies of the density, refractive index, dielectric constant, surface tension and several other properties of nitrobenzene.

In connection with an investigation of the entropies of some representative organic compounds containing nitrogen we have recently measured the heat capacity of liquid nitrobenzene over a continuous range from 0° to 26°C. The determinations were made by the Nernst method with an aneroid calorimeter[3] and represent average specific heats for temperature intervals of only 3° or 4°. While the systematic errors in the results thus obtained may possibly have been as great as 0.6 percent, the fortuitous errors, which are the important ones in the present argument, were certainly less than 0.30 percent in all cases. The sample of nitrobenzene employed was obtained from a C. P. Eastman material by eight successive fractional crystallizations. Its melting point, determined both by a copper-constantan thermocouple in the course of the heat capacity measurements and by a mercury thermometer which had been calibrated by the U. S. Bureau of Standards, was 5.65° (±0.05°).

Our experimental results are given in columns 1 and 2 of Table I and are also represented graphically in Fig. 1. As can be readily seen, they deviate only very slightly and in a fortuitous manner from the straight line which represents the equation, $C_p = 0.3460 + 0.00066t$. The values calculated by this equation are also given in the third column of the table in order to facilitate comparison with the experimental data. The liquid can be readily cooled several degrees below the freezing point and the first two experimental results refer to measurements made upon our sample in this undercooled condition.

TABLE I. *Specific heat data for liquid nitrobenzene.*

Average Temp. (°C)	C_p observed (cal./g)	C_p calculated (cal./g)
1.95	0.3474	0.3473
3.30	0.3484	0.3482
7.42	0.3501	0.3509
11.60	0.3543	0.3537
15.94	0.3561	0.3565
20.11	0.3598	0.3593
24.25	0.3616	0.3620

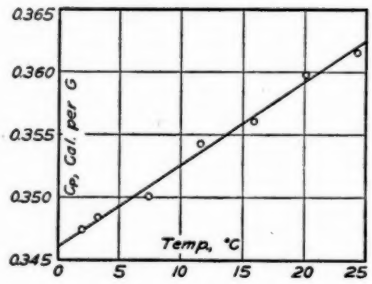

FIG. 1. A plot of the specific heat data for liquid nitrobenzene.

[1] (a) Mazur, Nature **126**, 993 (1930); **127**, 741, 893 (1931); Acta. Phys. Pol. **1**, 53 (1932); (b) Wolfke and Mazur, Zeits. f. Physik **74**, 110 (1932); Acta Phys. Pol. **1**, 71 (1932); (c) Wolfke and Ziemecki, Acta. Phys. Pol. **1**, 271 (1932).

[2] Lind and Young, J. Chem. Phys. **1**, 266 (1933); Wellm, Zeits. f. physik. Chemie **B19**, 113 (1932); Cohen and te Boekhorst, Proc. Acad. Sci. Amsterdam **35**, 1016 (1932).

[3] Parks, J. Am. Chem. Soc. **47**, 338 (1925).

It is quite evident that our heat capacity results show no discontinuity in the neighborhood of 9.6° and no sign of a heat of transition. In our procedure the latter would naturally have been included in either the measurement corresponding to an average temperature of 7.4° or that for 11.6°, as the series of measurements left no temperature gaps between 0° and 26°. Therefore we can see no basis for the claim that pure nitrobenzene exists in two allotropic liquid forms.

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May 11, 1934.

The Significance of the Activation Energy of Collision

Acoustical measurements have established that the rate of vibrational energy exchange is in general strongly dependent on temperature.[1] In order to describe this the term "activation energy of collision" has been employed,[2] and this quantity appears to be of the order of one to three $h\nu$ where ν is the vibration frequency of the molecules in the experiments so far reported. I wish to report in this letter the preliminary result of a theoretical investigation which has attempted to give the "activation energy of collision" a more precise significance.

At first the excited and exciting molecules were considered held at a fixed distance, and then the relative kinetic energy was allowed to enter as a perburbation giving rise to an exchange of translational and vibrational energy. This led to two simultaneous differential equations for the eigenfunctions of the excited and the unexcited molecules. To solve these to a first approximation plane wave functions which vanished inside the kinetic theory diameter were introduced. This permitted a comparison between the outward flow of excited molecules with a normalized incoming wave of unexcited molecules. This gave for a collision energy E a probability for the exchange of a vibrational quantum proportional to $E^{1/2}(E-H\nu)^{5/2}$. This treatment differs from that given by Rice[3] in that the wave function of the internal coordinates includes as a parameter, a fixed value of the distance of separation due to the clamping of the molecules. It obviates as well the paradoxical approximation of adiabatic approach implied in an extension of the treatment of Kallman and London[2, 4] to the conversion of translational into vibrational energy.

When integrated over all energies the temperature dependence of the yield is nearly proportional to the fourth power of the temperature times the usual factor $e^{-h\nu/kt}$. Expressed as an activation energy this is approximately $4kt$, which agrees well with the experimental values for carbon dioxide, carbon disulfide, etc. The second order effects such as the softening of the bonds at close approach, the effect of repulsion on the eigenfunctions previous to the point where they vanish, and the shielding by other atoms in polyatomic molecules would tend to increase this temperature dependence. The absolute magnitude of the yield was of the order of $10^{-4}-10^{-7}$ per collision depending upon the type of molecule. This is also in agreement with experiment.

HILLARD B. HUNTINGTON

Princeton University,
Princeton, New Jersey,
June 1, 1934.

[1] Henry, Proc. Camb. Phil. Soc. **28**, 249 (1932); Richards and Reid, Nature **130**, 739 (1932); J. Chem. Phys. **2**, 193, 206 (1934).

[2] Richards, J. Chem. Phys. **1**, 874 (1933).

[3] Rice, J. Am. Chem. Soc. **54**, 4559 (1932).

[4] Kallman and London, Zeits. f. physik. Chemie **B2**, 207 (1929).

Photo-Dissociation of the Vapors of Organo-Metallic Compounds

The photochemistry of the simplest organo-metallic compounds of the type MR_n (M = metal, R = CH_3, C_2H_5, C_6H_5) has not as yet received due attention. Only one observation may be cited, namely that of Berthelot and Gaudechon,[1] who found that liquid $Zn(C_2H_5)_2$ illuminated by a quartz mercury arc decomposes rapidly into ethane and zinc metal. We expect in fact that less energy is needed to disrupt the bond M−C than the bond C−C; therefore photochemical reactions can be induced by smaller quanta such as those lying in the nearer ultraviolet.

A study of these compounds was therefore undertaken in this laboratory. Some of the results obtained are given here.

First, the absorption spectra of $Hg(CH_3)_2$, $Zn(CH_3)_2$ and $Pb(C_2H_5)_4$ were studied. These substances are very volatile. A structure in the absorption spectrum of $Hg(CH_3)_2$ could be detected only when this liquid was frozen down to −150°C. At room temperature the vapor pressure is so high that all the ultraviolet is completely absorbed.

The absorption spectrum of $Hg(CH_3)_2$ consists of a progression of diffuse bands in the region 2100–1970A. The spacing of these bands is equal to 350 cm^{-1} and represents presumably the vibration quantum of one of the valence modes of vibration of the mercury atom in the upper electronic state of the molecule. From the Raman spectrum the valence vibration frequencies of the Zn atom in the ground state of the $Zn(CH_3)_2$ molecule are known to be 506 and 617 cm^{-1}.[2] For $Hg(CH_3)_2$ no corresponding data are available, but the order of magnitude must be the same.

The electronic transition in the $Hg(CH_3)_2$ molecule is equal to 47,044 cm^{-1} or 5.8 e.v.

[1] Berthelot and Gaudechon, C. R. **156**, 1245 (1913).

[2] S. Venkateswaran, Ind. J. Phys. **5**, 145 (1930).

Besides this band spectrum a continuous absorption down to 2800A is observed. The potential energy curve attained in the absorption act must be evidently a steep curve of repulsion. The photo-dissociation process produced is assumed to be:

$$h\nu + Hg(CH_3)_2 \rightarrow CH_3 + HgCH_3.$$

The curve of repulsion belongs presumably to the ground electronic state of the molecule and a large surplus of kinetic energy amounting to 50 kcal. is imparted to the products of photo-dissociation. The existence of such a curve explains also the diffuseness of the band spectrum.

To test definitely the possibility of a photo-dissociation process with the rupture of the bond Hg−C, the behavior of the compounds $(CH_3)HgI$ and $(CH_3)HgBr$ was studied. It was demonstrated previously that under the action of suitable light quanta the molecules $Hg(Hal)_2$ can be split up according to the scheme:

$$h\nu + Hal - Hg - Hal \rightarrow Hal + Hg\ Hal^*$$

where Hg Hal* is an excited molecule HgI or Hg Br emitting its characteristic spectrum.[3] By analogy we expect this to be the case also for the methyl-halogen compounds of mercury.

In fact it was found that when diluted vapors of $(CH_3)HgI$ or $(CH_3)Hg\ Br$ are illiminated by short ultraviolet light, spectra belonging to excited Hg Hal molecules are emitted. From this and a detailed analysis of the experiments, the photo-dissociation:

$$h\nu + (CH_3)Hg\ Hal \rightarrow CH_3 + Hg\ Hal^*$$

was ascertained.

The strength of the bond Hg−C evaluated from these experiments is of the order of 60 kcal. per mole.

For $Zn(CH_3)_2$ and $Pb(C_2H_5)_4$ only a continuous absorption spectrum was observed.

The vapors of these latter substances are readily decomposed by ultraviolet light with the formation of metallic dust on the path of the light beam.

Further details and an analysis of the results obtained will be published soon elsewhere.

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[3] A. Terenin, Zeits. f. Physik **44**, 713 (1927).

The Exchange Reaction of Hydrogen and Deuterium Oxide

The exchange of deuterium between hydrogen and deuterium oxide molecules has been shown to take place at high temperatures.[1] There is now available sufficient spectroscopic data to calculate the equilibrium constant of the reaction.

The constant for

$$H_2 + HDO \rightleftarrows HD + H_2O$$

is given by

$$K = \frac{f_{H_2O} f_{HD}}{f_{HDO} f_{H_2}}$$

where the f quantities are the distribution functions for the several molecules. For water and hydrogen the functions are

$$f_{H_2O} = \left(\exp + \frac{\zeta_{H_2O}}{kT}\right) \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2(8\pi^3 ABC)^{\frac{1}{2}}}{2h^3} \times (kT)^{\frac{3}{2}} \Pi_{i=k,l,m} \frac{1}{1-\exp -\frac{h\nu i}{kT}}$$

$$f_{H_2} = \left(\exp + \frac{\zeta_{H_2}}{kT}\right) \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \Sigma p \exp -\frac{Ev, j}{kT}.$$

The function for HDO is similar to that for H_2O except that no symmetry correction is required and the statistical weight factor is 6 instead of 4. The function f_{HD} is similar to f_{H_2}, p being the weight factor. These more exact data for the H_2 and HD molecules are available from the work of Urey and Rittenberg.[2] Calculations were made for the additional temperatures necessary. The moments of inertia (ABC) and fundamental vibration frequencies for H_2O and HDO were obtained from Topley and Eyring.[3]

TABLE I. *Equilibrium constants for the reaction.* $HDO + H_2 \rightleftarrows H_2O + HD$

T	k	T	k
300	1.59	700	0.74
400	1.09	800	.68
500	0.93	900	.64
600	.81		

Here it is necessary to use the approximations for the vibrational energy. ζ is the energy of the molecule in its lowest state. The calculated values of the equilibrium constant are given in Table I. This temperature dependence of the equilibrium constant is almost entirely due to the effect of the temperature in the exponential term for the zero point energies.

Experiments were carried out in a Pyrex container of 1565 cc capacity and maintained at constant temperature by a sulfur vapor bath. The vessel containing one cc of liquid water with deuterium was filled with hydrogen to one atmosphere at room temperature. The rate of the reaction is illustrated in the following data.

Temp. = 495°C							
time in hrs.	0	19⅓	46	86½			
% D in water sample	14.66	11.62	9.93	9.01			
Temp. = 507°C							
time in hrs.	0	2	4	8	22	44⅓	6 days
% D in water sample	6.25	5.79	5.69	5.63	4.46	3.64	3.54

[1] Crist and Dalin, J. Chem. Phys. **1**, 677 (1934).
[2] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).
[3] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

From these data the time required for equilibrium could be estimated. The measurements cannot be considered reliable for rate studies since the effect of a darkening of the vessel could not be determined. This study is now being continued in quartz apparatus. The analyses were made by means of the interferometer.[4]

TABLE II. *Equilibrium data for* $HDO+H_2 \rightleftarrows H_2O+HD$.

No.	Temp. in °C	% HDO in water	% HD in hydrogen	k
1	526	12.88	9.46	0.71
2	526	6.74	4.56	.66
3	530	6.10	4.68	.76
4*	520	7.42	3.66	.48

* This is probably not at equilibrium due to a temperature fluctuation during the run.

The equilibria data are contained in Table II. In all but No. 1 the original mixture was HDO, H_2O+H_2 while in 1 the amounts of HDO and HD in the original mixture were the same. Thus the equilibrium was approached from both sides. The hydrogen sample was converted to water by passing over copper oxide and then analyzed.

According to the results of Table I the variations in k found here are to be ascribed to experimental error.

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[4] Crist, Murphy and Urey, J. Chem. Phys. **2**, 112 (1934).